HENRY CLIFTON SORBY, F.R.S.

". . to him is due the pioneer's honor."

AN INTRODUCTION

TO

PHYSICAL METALLURGY

BY

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To

ALBERT SAUVEUR

PREFACE

This book—a brief exposition of fundamental physical metallurgical principles—is an outgrowth of a course of lectures which I have given at Harvard University for some years past. The students electing the course have been, for the most part, postgraduate engineers, metallurgists and mechanical engineers predominating—students in the Graduate School of Engineering. Recently, the course has been opened to certain qualified undergraduates in Harvard College, and the group electing it has proved to be still more diverse in interests. Experience of some years with this rather heterogeneous group indicated that there was no introductory text in physical metallurgy which was at once sufficiently specific and fundamental for those who were to continue in the science, yet interesting and comprehensive enough for those seeking a general knowledge of the subject and whose active acquaintance with it would likely end with the course. This book was written to fill that need.

Physical metallurgy has developed, in recent years, into a somewhat comprehensive science. Long after Sorby's time, metallography—as the science was then called—continued to have its major interest in metallic microscopy and in the correlating of microstructure with mechanical properties, particularly of the industrial alloys. This notion of what the peculiar field of the science was, however, no longer holds, for any phase of metallic structure or behavior is now considered—and quite rightly—the proper concern of the physical metallurgist. Such diverse problems as those connected with the physics of metal crystals—their fine structure, their behavior under stress and temperature, etc.; the electrochemical problem of corrosion; the physical chemical problem of nonequilibrium in alloy systems; and many others that one might name are now conceded to be within the province of the physical metallurgist. As a consequence, he needs to be somewhat of a physicist, a physical chemist, and a crystallographer, as well as an engineer, for his

applied science draws largely on these fundamental physical sciences for its sustenance and development. These facts have been kept constantly in mind during the writing of this book.

The number of those to whom credit is due, because of one circumstance or another, is so great that only a general acknowledgment of my debt seems possible. Many photomicrographs and many data of former students have been included in the text, with credit in each case. To Dr. E. L. Reed, research metallurgist at the Watertown Arsenal, special thanks are due for the use of many of his fine photomicrographs.

Dr. Albert Sauveur, Gordon McKay Professor of Metallurgy and Metallography, Emeritus, Harvard University, and Dr. George B. Waterhouse, Professor of Metallurgy, the Massachusetts Institute of Technology, both read the manuscript before it was submitted to the publishers. My sincere thanks is theirs, for I know the hours of their busy lives which were required to examine critically what, I am afraid, was not always an easy-reading copy. I appreciate their interest in my undertaking, and I was happy to listen to, and to act upon, their suggestions. I appreciate also the interest taken in my book by Dean Harry E. Clifford of the Graduate School of Engineering of Harvard. His long editorial experience made his suggestions doubly valuable.

L. R. VAN WERT

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AN INTRODUCTION TO PHYSICAL METALLURGY

INTRODUCTION

"To react against these (taboos), to tame them and subdue them to its ends, humanity sought an auxiliary in a false science, magic, which is the mother of all true sciences."

"When once magic had become a profession, . . . , the magician had perforce to produce some happy effects, calculated to commend recognition and respect; so the charlatan became a physician, astronomer, metallurgist."

—REINACH.

The genesis of the metallurgic art may be thus and so, and may have occurred in the comparatively recent time of which Reinach in his "Orpheus" writes, but surely man's acquaintance with the metals is much antecedent to his development of a processing technique; indeed, to find the beginnings of that acquaintance, one must go back to the very childhood of the race. Obviously, one's notions of a matter of such antiquity are largely conjectural.

As the seemingly interminably long Stone Age at last drew to its close, the "animal which is man" had become something quite apart from the rest of "earth's children," for he alone had learned how to make for his own use implements of flint and bone. Other animals might, after a fashion, *use* the simple tools that nature had grudgingly provided, but only man could make his own. Man's uniqueness as the sole tool-making animal of creation might yet have come to naught had not some unnamed genius, toward the end of the Stone Age, discovered the plastic metals, materials infinitely more responsive to man's lately acquired, yet really deft craftsmanship. With these new ductile, yet hard and strong substances, early man continued to work his artistry, producing ornaments and implements, of aesthetic and serviceable qualities, altogether impossible of attainment in a less

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versatile material. With his discovery of the metals, man was off to a fresh start along the long road that has led him to his present high place in the natural world.

Thus, from early Pleistocene time, but more especially after man's emergence from the prehistoric phase of his development, the metals have played an increasingly significant role in his material affairs—in the providing of means of shelter, in the building and equipping of ways of transportation and communication, in the manufacture of armament, and as the chief material from which he fabricates the tools, appliances, and machines that multiply a thousand-fold the labor of his hands. It is, of course, needless to point out the importance of the metals in man's present economy. Our own time has sometimes been called the "metal age," but it is hardly possible that the essential quality of a culture so complex and diverse in interests as is ours can be contained in so small a compass; rather the intent of the term is simply to do, what good archaeological practice approves, *viz.*, to name and define a culture in terms of the principal material of which contemporary man makes his tools.

The story of the metals and man is thus an ancient one, and with so old a story there are, necessarily, many missing pages from the early chapters. What the first of these chapters would tell us we can only guess for time has obliterated all the material evidence. The discovery of the metals—when, where, and by whom, we do not know—is one of the really epochal events of man's unusually eventful career on this planet; it takes rank with such significant events as the first utilization of the cereal grains, the domestication of cattle, and the invention of an alphabet. As with these happenings, the discovery of the metals brought one notable epoch in the race's history to an end and ushered in another—our present—era.

A somewhat later chapter in history properly begins with the discovery of the methods of reducing metals from their ores. This notable advance in the metallurgic art by primitive man followed, as one result, an even more momentous happening—the discovery of fire, which has been described as "the most characteristic act of genius of which mankind can boast." Surely, no other single event has so profoundly shaped human destinies. One of the many far-reaching results of the discovery of fire was that it provided man with the means of unlocking the metal

treasures of the earth, where, in the form of refractory minerals, they had hitherto been unavailable. With the application of fire to metal reduction (smelting), the art of metallurgy really began, as the production of metallic materials, on any considerable scale, became for the first time a possibility. For man now was no longer dependent on the chance finding of meteoric fragments or terrestrial nuggets for his metal; in ores he had a dependable and inexhaustible source of supply. Moreover, his melting and smelting operations gave him metallic materials of varying properties, since he inadvertently alloyed with his metal certain constituents of the ore and fuel, and these affected his metal's properties. By long and painful experience, man learned that chemical composition was of considerable influence on his metallic product, and, in the same way, he learned how these impurities could be eliminated where they were harmful or, if helpful, how they could be deliberately increased. Thus, specific refining and alloying processes came into being.

The final phase in the history of the metals and man is concerned with the developments in the art (shortly to become the science) of metallurgy that have taken place in historical times. This is not the place to recite these developments in detail. For us it will be sufficient to note that these comparatively recent developments have been mainly in two directions. First, continuing with the methods of the older metallurgy, improvements have been made in the attempt (*a*) to secure more refined, more surely controllable, more mechanized, and cheaper methods of extraction, and (*b*) to build larger and more thermally efficient units of reduction, designed not only for the production of higher purity metal but also for the recovery and utilization of by-products. These developments belong to the field of production metallurgy, which is not our chief interest now.

Rather, our especial concern is in the second of the two directions in which metallurgy has made noteworthy progression, *viz.*, the study of the fundamental structure and properties of the metals and the metallic alloys. This phase of metal science—*metallography*, we now call it—dates only from 1864, when Sorby, an English scientist, reported on his work, begun a year previous, on the microstructure of the meteoric irons. This work was the natural consequence of a long and active interest on the part of this investigator in the microstructure of minerals.

Not till 1878, fourteen years later, did another report on work carried on in this field when Martens, in Germany, published his first paper. Thus, "to Dr. Sorby and to him alone"—as Dr. Sauveur has said[1]—"is due the pioneer's honor." Yet, the real impetus given to the use of the microscope as a tool for the study of metallic structure came as the result of two subsequent papers by Sorby, which he read before the Iron and Steel Institute (Great Britain) in 1886 and 1887. These two later contributions of Sorby, illustrated by many fine photomicrographs of iron and steel, aroused the attention of metallurgists to an extent that his pioneer paper did not, and from that time on metallic microscopy grew apace. The early workers in this field, other than Sorby and Martens, were Stead and Arnold in England, Osmond in France, and Howe and Sauveur in America.

In January, 1896, only a few months after the discovery of the X rays (by Röntgen in the fall of 1895), Dr. Albert Sauveur, at the Illinois Steel Company, used this unusually penetrating form of radiation in an attempt to detect internal flaws and defects in steel. This initial experiment was not a success, for the radiation produced by the crude methods then at hand lacked the quality necessary for the penetration of substances so opaque (dense) as the metals. It was, however, the first attempted experiment in metal radiography. In many fields of metal technology (welding, casting, etc.), radiographic methods are now of wide and important use.

Friedrich and Knipping's experimental verification, in 1912, of Laue's novel theory that, because the distances between the "rows" of the symmetrically spaced atoms of a crystal are of the magnitude of the wave lengths of X rays, a crystal should act as a three-dimensional diffraction grating for these rays, marks the beginning of the science of X ray crystal analysis. As we shall soon see, the metals are crystalline in character, and the recent application of X ray diffraction methods in the study of the fine structure of crystals has nowhere been more successful than with metal crystals. X ray metallography has revealed much of the enigmatic nature of metal structure and behavior.

The word "metal," like many another name of an everyday thing, is of an ancient etymological lineage. It comes to us

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[1] Quotation from the biographical sketch of Sorby by the Editor of the *Metallographist*, **3**, No. 2, April, 1900.

through the Latin *metallum*, from either the Greek noun *métallon* (*meta* = with + *allos* = another), signifying complexity (as of ores), or more likely, from the Greek verb *metallân*, to seek after, suggestive, as Rickard has observed, of ore prospecting. In either case, the use of the word was not originally confined to the metals alone but was applied more comprehensively to include also the minerals, ores, mines, mining, etc.

Man's age-long acquaintance with the metals presents an interesting, if somewhat disturbing, fact, *viz.*, he has known *of* the metals so long that the origin of the name is uncertain, yet, as we shall soon learn, he knows so little *about* them that their real nature is yet but vaguely understood. The reasons for this last unhappy circumstance are not hard to find. In the first place, one must remember that for many, many centuries man's only interest in the metals was utilitarian; all man knew, or cared, about the metals was that they possessed certain properties that made them useful; it has been only during the last fifty years that man has made any attempt to discover the essential nature and meaning of metallic behavior. Progress in this search has been beset by many obstacles. Experimental inquiry has often been hampered by the lack of adequate research tools, for in metal research as elsewhere investigative enterprises have, on occasion, had to wait on the invention or development of more precise analytic or measuring appliances or methods. For the metals are no structurally simple things. They are chemical elements whose individual atoms are built up in the usual intricate way of all atoms, in a way that atomic physics has yet fully to understand. But a metal's interatomic relationships—the manner of the bonding of its atoms to form a solid—is likewise as little understood. Apparently, it differs from either the true ionic or homopolar (covalent) types of bonding of other crystalline solids. Yet, without doubt, it is the peculiar bonding mechanism of the metals which provides, at least, one key to the enigma of "metallicity." As we shall see, our present notions of the electronic and atomic relationships that prevail in metallic substances are, in some cases, indefinite indeed.

The metal sciences may be classified into two major groups: To the first group belong such applied sciences as deal with the extraction of the metals from their ores, as: beneficiation of ores

(ore dressing), pyrometallurgy, hydrometallurgy, electrometallurgy, and the numerous refining processes used in conjunction therewith. Also properly included here are the several methods of recovery and treatment of metallurgical by-products, and again—for they are allied with the group—the processing methods and treatments as, for example, alloying, various types of casting operations, and heat and mechanical treatments. This rather comprehensive group of the metal sciences is obviously concerned with the reduction, refining, and otherwise preparing the metals, and, for this reason, the group is commonly designated *process*, *chemical*, or *extractive metallurgy*.

In the second major group of the metal sciences are included those studies that deal with the more scientific aspects of metal behavior. The metals are used in the arts and the industries because they possess certain desirable serviceable properties; for example, for many engineering purposes, the high hardness and strength of metal are essential qualities, while in the decorative and architectural arts the emphasis is more often laid on color and weathering behavior. It is of general knowledge that the physical properties of a metal—as, indeed, those of other substances—are wholly determined by that bonded complex of electrons, atoms, and crystals that go to make it up. Moreover, we know that this structural complex is by no means an unalterable affair, but rather one that can be changed, more or less, by man's device, that is to say, by suitable thermal, mechanical, chemical (alloying), or other means. From this alteration in structure necessarily ensues modification of properties. It is in *metallic structure, in the possible alteration thereof, and in the property changes resulting therefrom* that the sciences of the second group are mainly concerned. The name for this group of the metal sciences is *physical metallurgy*, or *metallography*.

In this book, we shall be interested in physical metallurgy in its broadest aspects, and we shall begin our study of the subject by critically examining the "pure" metals in the light of their more characteristic properties and behavior, in an endeavor to arrive at an adequate notion of the *metallic state*.

CHAPTER I

WHAT IS A METAL?

"Thou hast asked a hard thing."

—2 KINGS 10.

"Metal is a mineral body, by nature liquid or somewhat hard."

—AGRICOLA (1546).

The Metallic State.—The title question, like so many other questions that one can ask concerning the nature of common things, is not easily answered. Admittedly, there is no simple yet adequate definition of a metal. Many of the ninety odd chemical elements are obviously metals—in fact, most of them are—others are as obviously nonmetals, but by what token one makes the distinction between the two groups, one cannot be so sure. There are a few elements, also, that partake of the nature of both metals and nonmetals, under many—indeed, under most —conditions they seem metallic enough, but on occasion their behavior is decidedly nonmetallic. These *metalloids*, as they are sometimes called, add a further difficulty in the attempt to frame a satisfactory definition of the metallic state.

We shall tentatively describe the metals as chemical elements possessing certain specific properties which appear to be characteristic of such elements; in other words, we shall now define a metal on the basis of the more obvious properties of the group. While this description of a metal may lack the preciseness of an exact definition, it is not without some definitive value, for experience with metallic behavior, either in the laboratory or under actual service conditions in industry, teaches us that the metals do really possess some important properties not possessed—at least, to the same extent—by the nonmetallic elements. This is, indeed, true despite the equally patent fact that these peculiarly metallic properties are shared unequally by the several individuals of the group, that some of the metals are more metallic than others. The circumstance of varying metallicity among the so-called metallic elements accounts for (though it does not

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explain) the existence of the often enigmatic borderline metals, those elements which under many circumstances appear so little metallic in their conduct that one may well question their fundamental metallic nature.

A practical discussion of the properties of the metals is reserved till later (Chap. II, and again in Chap. VI), but of those properties characteristically metallic enough to serve to set the group apart from the other elements of the periodic classification, and to give it an adjectival distinction, something will now be said. The characteristically metallic properties include:

   a. High hardness and strength.
   b. Plasticity.
   c. Certain electrical and thermal properties and effects.

a. High Hardness and Strength.—Casual observation tells us that the metals are relatively hard and strong substances. They are strong because we know that they effectively resist rupture and that this is true whether the forces tending to rupture are in tension, compression, torsion, or in shear. We know too that they are hard because they permit, only with considerable difficulty, penetration by another and harder body, which is, perhaps, the best way to appraise hardness. There is apparently something peculiarly tenacious and cohesive in the metallic type of (atom) bonding which makes most metals oppose, in an unusually efficient manner, external forces which would, in effect, tear the atoms apart or at least displace them (or blocks of them) from their equilibrium positions. It would seem, then, that we have in high mechanical hardness and strength, *one* consequence of an internal structure peculiar to those elements we call metals.

b. Plasticity.—It is common knowledge also that some metals may be drawn into wire and rolled or hammered into sheet. As a matter of fact, the latter property was known to prehistoric man; with another property—color, for gold and copper it enabled him to distinguish between metal nuggets and friable pebbles of stream beds. The property which permits a metal to be drawn into wire is known as ductility, while that which makes it possible to roll it into sheet is called malleability. Neither is a simple property, but a composite in which strength is one element concerned. Another element is plasticity, the ability to flow under pressure. High ductility (or malleability) involves a suitable

combination of, and coordination between, strength and plasticity. A well-developed capacity to flow plastically, coupled with high strength, is a property of crystalline substances, notably the metals, presumably because of the peculiar manner of response of such substances to an applied stress. As we shall later learn, plastic flow in crystalline substances occurs principally through transcrystalline slip and not, as one might at first expect, by relative movement of the crystals themselves.

All crystals, including metal crystals, are distinguished from isotropic bodies (as wax) in that their constituent atoms are arranged in a regular and orderly fashion. Crystals possess a definite spacial pattern (space lattice), which is wholly lacking in isotropic substances. It is this regularity in structural arrangement which accounts for the way plastic flow occurs in the metals. We find, then, that it is again a structural feature which is responsible for another somewhat typical metallic property.

c. **Thermal and Electrical Properties.**—Of greater worth than either of the foregoing as criteria of the true character of a metal are thermal and electrical properties. While the mechanical properties mentioned are characteristically metallic, they are not exclusively so, for actually the metals share their strength and hardness properties with other crystalline substances (many of the rock minerals, for example), though it is true that these properties are generally better developed in the metal group than elsewhere.

In thermal and electrical properties we discover a group of properties which are, *in kind*, without question uniquely metallic. As is well known, the metals are exceptionally good electrical conductors. True, certain nonmetallics are too, though usually less so. It is, however, the manner—one is almost tempted to say, the "mechanism"—of electrical conduction, and not the fact itself, wherein lies a metal's uniqueness. A metal conducts the current electronically, that is to say, by the motion of electrons. There is no actual transfer of matter such as occurs in ionic conduction (in electrolysis or in ionized gases), where ions—charged particles of a finite mass—are the carriers of current. Electronic conduction seems, then, an exclusive metallic phenomenon[1] and is presumably the consequence of a distinctive

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[1] Many metallic compounds, as certain metallic oxides, nitrides, etc., also exhibit the property—an inherited character from the metal element.

feature of the metal lattice, *i.e.*, the "framework" on which the metal's atoms are arranged.

A metal is a chemical element and, as such, the structure of its atom conforms with atomic architecture generally. There is the nucleus, of net positive charge, relatively heavy but small, accounting for practically all of the atom's mass. Surrounding this are "shells of negative electrification" of such total charge as to equal the net positive charge of the nucleus. The atom is thus electrically neutral. The outer "shells" of the atom are essentially made up of *electrons*, indefinite sort of things, possessing mass and wave properties simultaneously,[1] and each having a mass of about $\frac{1}{1835}$ of that of the hydrogen atom (the lightest atom), and each of unit e negative charge. The nucleus, on the other hand, is made up of two kinds of charged particles: *protons*, particles carrying unit positive charges, and negatively charged electrons. The number of electrons actually resident with the protons within the nuclear portion of the atom is that which will neutralize about one-half of the total positive charge of the protons there; the remaining one-half, or thereabouts, of the electrons necessary for complete atomic neutrality is found in the above-mentioned outer "shells." Except for the atom's mass, these outer electrons give the atom most of its distinctive properties.

The outer electrons of the atom are built up in a series of concentric "shells" around the nucleus, with that number of electrons per "shell" (as two in the first, eight in the second, etc.) which permits of a symmetrical, and thus stable, distribution over the "shell." A stable configuration in *all* "shells" is, however, the case only of the atoms of the inert rare gases. Generally, there is an unfilled quota in the outermost "shell"; this results in an asymmetrical distribution of electrons over that particular "shell" and a certain degree of structural insufficiency to the atom as a whole. For this reason, such atoms tend either to acquire or to lose,

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[1] "It is not, . . . , that a physicist thinks of an electron as a particle on Mondays, Wednesdays, and Fridays, and as a wave on Tuesdays, Thursdays, and Saturdays, and on Sundays prays for a Messiah who will lead him back to the belief which he held on Mondays. The actual situation is quite different from that. He works with a mathematical theory which he visualizes for some purposes by means of the classical conception of a particle and for other purposes by means of the imagery of the wave theory." Oswald VEBLEN, Joseph Henry Lectures, Philosophical Society of Washington, 1934.

depending on circumstances, the number of electrons necessary to establish symmetry and chemical quiescence.   The number of electrons that must be gained, or lost (as the case may be) in order that structural stability may ensue denotes the principal *chemical valence* of the element.   Such in briefest form—and entirely without reference to the more important energy aspects of the atomic structure—is the picture of the atom, of both the metal and the nonmetal atom.   So far as one is able to tell, the metal atom, *per se*, differs in no structural sense from the nonmetal atom.   Perhaps one should not expect that it would.

Apparently, then, one must look outside the atom to find wherein a metal differs fundamentally from a nonmetal.   The extra-atomic source of "metallicity" is supposedly found in the peculiar bond—the so-called *metal bond*—of the metal atoms in the crystal lattice, to which reference has already been made, and in an additional, yet related lattice character, again uniquely possessed by the metallic elements, *viz.*, the presence of unattached, or *free*, electrons.   These free and seemingly autonomous electrons are not the ones described above, that is to say, they are neither the ones intimately associated with the protons in the nucleus, nor are they the ones found, at the time, in the shells surrounding the nucleus, but rather they are electrons possessing, temporarily at least, a detached, extra-atomic existence.   The presence of these free electrons in the lattice is a distinctive and fundamental feature of the metals; it is they which are supposedly responsible for the peculiarly metallic type of bonding, for electronic conduction, for the metals' high thermal conductivity, and for what other really unique aspects of metallic behavior exist.

It is not easy to get a simple and clear physical picture of the way these unattached electrons are related to the parent metal atoms, or to their lattice, but for the purpose of our elementary inquiry no precise notion is necessary.   Drude has thought that these electrons have the freedom of movement and other kinetic characteristics of the molecules of a perfect gas, while Sommerfeld would have them occupy fairly fixed and definite positions on a sort of lattice of their own.   But whether they are endowed with unlimited and haphazard motion, or whether more or less confined to lattice points, it is commonly agreed that in the presence of an electrical field the electrons concertedly move—a "drift," which gives rise to current flow.

For the present we shall be content with the bare statement of fact of high electrical conductivity in the metals, and with the assumption of its fundamental electronic nature, leaving all discussion of the practical significance of the phenomenon till Chap. II where conductivity is considered along with other properties of technical importance.[1]

In addition to conductance, the free electrons are held directly responsible for certain other distinctive metallic properties. These include various thermoelectric effects, emissivity phenomena, the property described as "contact potential," and the optical property of practically a total reflection of incident light. Only one of the first-named effects needs any description.

The thermoelectric effects of metallic materials, associated with the presence of unorthodoxly behaving electrons, are the Seebeck, the Peltier, and the Thompson effects.

a. The Seebeck Effect.—Seebeck (1832) discovered what is now a well-known phenomenon, *viz.*, if two dissimilar wires are connected in a closed circuit and the two junctions are maintained at different temperatures, an electric current will flow in the circuit. This phenomenon is the basis of the thermocouple unit of the thermoelectric method for the measurement of high temperatures. Two dissimilar metals (dissimilarity may be simply a question of appreciable composition differences) *M* and *N* (Fig. 1) are connected at two junctions *A* and *B*. At junction *A*, because of the phenomenon of "contact potential," electrons

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[1] Some interesting conduction phenomena, further evidence of the electronic character of conduction in the metals, might be briefly described:

a. Transverse (Longitudinal Hall) Effect: An increase in the longitudinal resistance in an electrical conductor placed at right angles to a magnetic field.

b. Hall Effect: Points along one edge of a rectangular electrical conductor are at a different electrical potential from those along the opposite edge when the conductor is placed in a transverse magnetic field.

c. Ettinghausen Effect: Points along one edge of an electrical conductor are at a different thermal potential (temperature) from those along the opposite edge when the conductor is placed in a transverse magnetic field.

d. Nernst Effect: Points along one edge of a rectangular thermal conductor are at a different electrical potential from those along the opposite edge when the conductor is placed in a transverse magnetic field.

e. Righi-Leduc Effect: Points along one edge of a rectangular thermal conductor are at a different thermal potential from those along the opposite edge when the conductor is placed in a transverse magnetic field.

tend to pass from one metal into the other, let us say, from M to N.

At junction B, at the same temperature as junction A, there is an equal electron pressure and an equal tendency for electrons to pass from metal M to metal N. The algebraic sum of the pressures is thus zero, and no current flows through the circuit. If, however, the temperature of the two junctions is different, the electron pressure at the junction of higher temperature (say, at junction A) will be greater than that at the lower temperature junction (the "cold junction"), the net

FIG. 1.—Two dissimilar metals, joined at junctions A and B.

contact potential then is of a finite value and a current will flow in the circuit (in the direction of the arrow).

The e.m.f. developed in the circuit is a function of the temperature difference of the two junctions,[1] or

$$E = E_A - E_B$$

where E_A is the e.m.f. developed at junction A, and E_B is that developed at junction B. Thus, the indicated e.m.f. is the algebraic sum of the two developed e.m.fs. and does not represent that of the hot junction alone. The simplest way to eliminate, in effect, the term E_B from the equation, that is, to make the indicated e.m.f. equal to the e.m.f. of the hot junction E_A, is to reduce the temperature of junction B to 0°C. Then the measured e.m.f. E is that due to the hot junction A above 0°C. This gives an e.m.f. which can be expressed in terms of temperature above 0°C.

b. The Peltier Effect.—This is the reverse of the Seebeck effect and may be stated as follows: When an electric current is allowed to flow across the junction of two dissimilar metals, heat is evolved when the current flows in one direction, and absorbed when it flows in the reverse direction. The reversal of the heat change distinguishes the Peltier effect from the more commonly observed heating effect of an electric current on a conductor (the Joule effect).

[1] Also of the materials of which the elements of the couple are made.

c. The Thompson Effect.—When a current flows down an unequally heated conductor, a transfer of heat takes place. In some metals (copper), when a current is passed from the hot to the cold end, heat is evolved and a current of heat flows down the wire in the direction of electric-current flow. In other metals (iron, for example) the reverse is the case, heat is absorbed and the direction of heat flow is opposite to that of electric-current flow.

Electron emission refers to the phenomenon of escape of electrons from metal surfaces. The stimuli inducing emission are, in general, three in number: an illumination of the metal by light of sufficiently low wave length; a heating of the metal to a sufficiently high temperature; and the presence of an external electric field of a sufficiently high strength. In all three cases, emissivity results from an increase in the kinetic energy (velocity) of the free electrons such that they can extricate themselves from the metal-lattice entanglement and actually clear the metal-surface barrier. When outside the metal, the electrons possess a quite independent existence, and because they are charged particles, they can be given direction and velocity by a proper electric field.

The process of electron emission by incident light of high frequency is known as *photoelectric emission;* the interesting fact concerning this phenomenon is that no matter how intense the radiation may be, if its frequency be not above a certain minimum value (the threshold frequency), emission will not take place.

A second type of electron emissivity, and one where a high temperature is the stimulus, is known as *thermionic emission.* This phenomenon forms the basis of most kinds of electron tubes, as, for instance, radio tubes and X ray (filament type) tubes. The high temperature of the glowing metal filament imparts to the electrons a velocity sufficiently high to enable certain of those momentarily advantageously located to detach themselves from the metal lattice and to escape free from the surface. Thermionic emission is an endothermic process and is analogous to vaporization where, at the boiling point, the molecules of a liquid acquire the necessary kinetic energy to permit them to leave the liquid.

The same sort of electron emission can occur through electron "extraction" from metal surfaces by intense electrical fields.

Still another variety of electronic phenomena, though related to the thermoelectric effects mentioned earlier, is *contact electricity*. The essential effect of this phenomenon—and this has already been alluded to—is that when two different metals are simply placed in contact, the one acquires a positive charge and the other a negative one, indicating that electrons have actually passed from the one to the other.

Summary.—The source of a metal's strength and plastic properties is found in its lattice structure, and in the manner of the bonding of the atoms in that lattice. The peculiar electrical and thermal properties of the metals, including many interrelated thermomagnetoelectrical phenomena, provide the factual basis of "metallicity," the explanation of these properties and effects, *i.e.*, general metallic behavior, by the assumption of free electrons within the metal lattice, completes, as far as the simple metals are concerned, the present notion of the metallic state.

We shall soon learn, however—something that we may, in fact, already know—that the simple metals do not constitute all of the known metallic substances. Many of these latter are even more intriguing to the student of metal physics—and more useful generally—than the metals themselves. On another occasion, we shall attempt to bring these less simple metallic materials within the meaning of the metallic state, by claiming for them, in *kind,* the lattice, linkage, and electronic characteristics of the pure metals.

CHAPTER II

THE METALS AND THEIR PROPERTIES

As a starting point in our discussion of the important technical properties of the metals, reference is again made to the fact that metals are chemical elements, that, in fact, they constitute the majority of the 92 elements that Mendeleeff has arranged into what is commonly known as the periodic table. In the usual form of this classification of the elements, each of the eight columns is occupied by equivalent elements, that is to say, by elements of like disparity in valence electrons. Valence, like other atomic properties, is periodic.

Not generally so, however, are many of those properties, as plasticity, strength, hardness, etc.—the so-called structural and granular properties—which find their origin chiefly in the crystalline units of matter. Thus, the orthodox form of the periodic table shows, on casual examination, little that would lead one to believe that the periodic grouping bears any significant relation to the more technically important physical and mechanical properties. But by separating subgroups A and B of main groups I to VII, inclusive, as is done (after Guertler-Leitgebel) in Fig. 2, one gets a quite satisfactory classification of the metallic elements into similar property groups; at the same time, the significant periodic feature of Mendeleeff's original classification is, in effect, retained.

This modification of the periodic table gives five general metal groups of somewhat similar properties. These are as follows:

a. The light metals.......................... Li, Be, Na, Mg, Al, Si, K, Ca, Se.

b. The heavy, brittle metals of high melting point Ti, V, Cr, Mn, Zr, Nb.

c. The heavy, ductile metals of high melting point Fe, Co, Ni, Cu, Mo, Ma, Ru, Rh, Pd, Ag, Hf, Ta, W, Re, Os, Ir, Pt, Au, Th, Pa, U.

d. The heavy metals of low melting point....... Zn, Gr, Ge, As, Cd, In, Sn, Sb, Hg, Tl, Pb, Bi, Po.

Non-metals
Inert gases

Non-metals

Transition elements

High-melting heavy metals

Low-melting heavy metals

Strong electropositive metals
Rare earths:

Light metals

The numbers in front of the chemical symbols represent the atomic numbers; those following, the atomic weights The geometric figures indicate the crystal structure at room temperature

☐ = face-centered cubic   ◉ = body-centered cubic   ⬡ = hexagon   ◇ = rhombohedral   ☐ = tetragonal   ☐ = diamond lattice   α, β = modification

Fig. 2.—Periodic system of the elements. (*Guertler-Leitgebel.*)

e. The strong, electropositive metals........... Rh, Sr, Cs, Ba, Ra, Ac,
                                                                    and the Rare Earths.

Including the rare earths, there are seventy odd elements that may be properly considered metallic; somewhat over one-half of these have, at present, no industrial importance, i.e., they are not used either as metals or in the alloyed condition.   Those metals of any industrial importance—a matter of some thirty— include: beryllium, magnesium, aluminum, silicon, and calcium, all of Group *a*; titanium, vanadium, chromium, manganese, and zirconium, of Group *b*; iron, nickel, cobalt, copper, molybdenum, palladium, silver, tantalum, tungsten, platinum, gold, and uranium, of Group *c*; and zinc, arsenic, cadmium, tin, antimony, mercury, lead, and bismuth, of Group *d*.   No Group *e* metals are included.

Of the above metals, about ten are of the greatest usefulness in the arts and industries.   These are aluminum of Group *a*; iron, nickel, copper, gold, and silver of Group *c*; and zinc, tin, and lead of Group *d*.   The remaining score or so metals are used in limited quantities only, principally as minor constituents in alloys.

One may well wonder what has determined this choice—why it is that so few metals, relatively, have been singled out for preferment.   A first consideration, obviously, is the matter of natural occurrence.   Many of the metals—the rare earths, for example—are exceedingly rare.   Others are less so, yet the limited amounts available would preclude them from any extensive use.   On the other hand, there are a number of metallic elements of very limited practical application whose natural occurrence is widespread and considerable.   Silicon is one. Over one-quarter of the earth's crust is this element; yet, as everyone knows, silicon is not a widely used metal.   The refractory character of its principal mineral, the oxide, SiO_2, presents considerable but not insurmountable difficulties in its reduction. But the real reason for the relative unimportance of silicon as an industrial metal is its want of well-developed serviceable properties.   It is not a particularly strong metal; and it is not plastic or tough.   Lacking any considerable ductility or malleability, it cannot be readily fabricated.   Moreover, it is not an especially good conductor of heat or electricity.   What is true of silicon holds, to a greater or lesser degree, for about 20 other metals.

All lack, in some large measure, some or all of the important property requirements demanded by most industrial and engineering uses and applications. As indicated previously, these metals find their principal use in alloys, where as a minor constituent they confer specific rather than general properties on the alloy.

In Chap. I, mention was made of certain metallic properties of a greater or lesser significance in determining what a metal is. We shall now discuss properties somewhat more comprehensively, and from a more practical point of view. The properties of a metal, we find, may be classified, *as to origin*, into three groups:

a. Atomic Properties.—This group of properties is accounted for by difference in individual atoms with respect to volume, valence, etc.

b. Structure Properties.—Properties of this group are determined by the way the atoms are put together. The difference between allotropic forms of the same element, *e.g.*, iron, is a structure property; the way metals respond to deformation stresses is another.

c. Granular Properties.—These properties are determined by a still larger unit of organization, *viz.*, by the way the several crystalline grains go together to form the mass. Those mechanical properties of a metal which are influenced by grain size, orientation of the grains, etc., belong here.

Several individual properties of the metals which are of particular scientific and practical interest will now be discussed; the first of these is crystallinity.

Crystallinity.—Of considerable scientific interest, and of greatest technical importance, is the fact that the metals are crystalline in their nature. This fact results from the circumstance that when a metal passes from the liquid to the solid state, or when it freezes—as we ordinarily say—it forms crystals. Thus it is that any particular piece of ordinary solid metal is a crystalline aggregate, a mass of a great many small crystals tightly bound together.

The external appearance of a well-formed crystal is familiar enough. Its most patent feature is its geometrical shape which is defined by more or less perfectly formed faces (facets), intersecting at precise angles. Though most in evidence, this assumption of a geometrical form is, in fact, not the essential quality of crystallinity; with a crystal, as with much else of the physical universe, one must look below the surface of things to find the essence. Actually, the distinctive and peculiar property of crystalline matter is a regularity and order of atomic spacing;

the atoms of a crystal are arranged in a perfectly definite fashion and according to a specific design, and it is this internal architecture—the *space lattice*—which distinguishes, in a fundamental manner, crystalline from rigid, noncrystalline bodies, as, for example, glass.[1] This definite spacing and regular arrangement of the constituent atoms of a crystal explain the unique properties of a crystal, including its optical and X ray diffraction properties, its anisotropism, its peculiar manner of plastic flow, and—whenever in evidence—its regular external form.

Rarely, however, does a metal crystal (as indeed does that of any rock mineral) have the opportunity to develop an outward form in conformity with an internal symmetrical spacing of the atoms. The usual conditions under which a crystal forms, *i.e.*, from a melt where many other crystals are growing, simultaneously and competitively, prevent it. Its final shape is more often determined by its abutting neighbors than by its own crystallizing habit. Crystals lacking a regular crystal form by reason of circumstances of birth and growth are called *allotriomorphic* crystals; those forming under less usual, but more favorable conditions, and where development of a regular external form becomes possible, are designated *idiomorphic* crystals. Most metals are made up wholly of crystals of the former variety, for only very rarely does solidification (of metal melts) permit anything like idiomorphic crystals to form. Like museum specimens of the rock minerals, idiomorphic metal crystals are of interest largely because of their rarity.

It cannot be too strongly emphasized, however, that allotriomorphism is imposed from without, that it is an entirely exopathic condition—as one would say, if a crystal were a living organism. On first thought, one might suppose that the external "imperfectness" of an allotriomorphic crystal results from some miscarriage of the crystallizing process, but this is not so, for, for all their formless exteriority, allotriomorphic crystals are none the less crystalline. The failure to develop an outward form in accordance with an internal pattern vitiates, in no one essential partic-

[1] Substances lacking a regularity in atomic arrangement, thus whose properties are nondirectional, are called *isotropic* substances. All gases, all liquids, and such rigid materials as glass or wax are examples. Crystalline solids are anisotropic; a definite arrangement of the atoms on a lattice introduces the possibility of directional properties.

ular, the fundamental character of a crystal. In structure, in properties—indeed, in all features save a supervenient form—they differ in no way from their more favored idiomorphic brethren.

Solidification (crystallization) involves a significant energy change. As is well known, in all liquids, including the molten metals, the molecules (or atoms) occupy no fixed positions relative to one another; all are free to move in much the same way as the molecules of a gas, with, of course, comparatively shorter "mean free paths." This restriction is due to the relatively greater attraction between the molecules of a liquid than of a gas; thus, liquids are more viscous than gases. But like gases, liquids are isotropic substances.
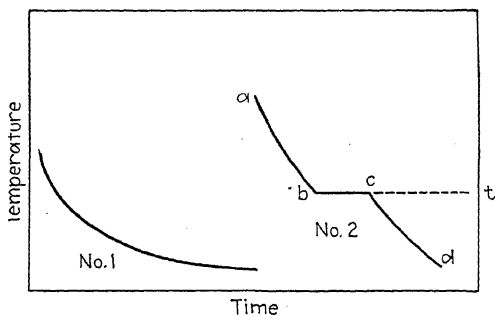
Fig. 3.—Cooling curve of (1) isotropic substance, and of (2) a crystalline solid (metal).

When some liquids, as, for example, fused glass or melted wax, are slowly cooled, they change imperceptibly from a liquid of low viscosity to one which is extremely high, *i.e.*, they congeal or "set"; they do not really solidify or freeze in the correct meaning of these terms. Thus, glass or wax, at ordinary temperatures, while rigid enough, are in reality not solids at all; they are merely extremely viscous, *undercooled* liquids. And being liquids, they are isotropic.

If we should determine the time-temperature curve of the cooling of either of these two substances, by merely noting while the substance cools, its temperature at the end of equal time periods, we would get a curve that would look something like the first curve in Fig. 3. This, as one can see, is a perfectly smooth and regular curve, showing nothing that would indicate

nonuniformities in the cooling rate. It is true that the curve "flattens out" as cooling proceeds, but this is obviously due to a slower rate of heat transfer from the substance to its environment as its temperature more nearly approaches that of the latter. Quite plainly, the curve represents the cooling of a material whose cooling process involves nothing more or less than a simple loss of heat energy.

But the behavior of most liquids (molten metals and alloys, fused salts, water, etc.), when cooling down to a temperature where they become solid, is a different story. These liquids actually freeze when they reach a certain temperature, *i.e.*, they become crystallized solids at their freezing points. Above their freezing points they are liquids; below, they are solids, and (for pure substances) the liquid-solid change is sudden and sharp, not gradual and imperceptible. Microscopical and X ray examination of the resulting solid would show that it is crystalline in character, an aggregate of many anisotropic crystals. It is, of a truth, a solid, not merely a rigid body that has become so by reason of an extremely high viscosity.

Moreover, a comparison of the cooling curves (No. 1 of Fig. 3 with No. 2 of that figure) of the two substances reveals that some difference, of a fundamental thermophysical nature, exists between the process of solidification by crystallization and the formation of a pseudo-solid by the undercooling of a liquid. Differing from the No. 1 curve, there are three portions to curve No. 2. At temperature t, the freezing point, there is a discontinuity in the latter curve, whereas the former curve is quite regular in contour. The upper part of curve No. 2, a–b, represents the cooling of the molten substance (say, a metal) down to freezing; strictly speaking, it is the only portion of this curve that is comparable to curve No. 1. The portion c–d represents the cooling of the solid metal down to room temperatures, and b–c, the horizontal portion of the curve, represents the time interval during which freezing occurs. During this time, the atoms of the melt are changing from a condition of haphazard motion to one wherein they take up definite and fixed positions, forming the so-called space lattice of the solid metal. The atoms of the liquid state, because of their motion, possess a certain kinetic energy, and in assuming fixed positions in a lattice, this energy is dissipated; thus, as is well known, the condition of the solid state

is one of less internal energy than the liquid state, and solidification becomes an exothermic process. The difference in the energy content of the atoms of the liquid state and that of the atoms of the solid state is the *latent heat of fusion;* it is a definite calorific quantity for a unit mass of any substance. If freezing is an exothermic process, then the reverse process, melting, is endothermic, and the energy (heat) input required to melt a given mass of a substance, as a metal for example, is exactly that released at the time of solidification. This is the explanation why there is no fall in temperature during the actual solidification, why the *b–c* portion of curve No. 2 is horizontal, *i.e.*, parallel to the time axis.

On the basis of axial relationships, crystallographers distinguish six distinct crystal types.[1] Only three of these are of any interest metallographically, but to show wherein these three differ from the rest, all six are listed with their defining attributes. These are, as follows:

I. *Cubic, or Isometric:* The three axes (of reference) are of equal length, and are at right angles to one another.

II. *Tetragonal:* Two axes only are of equal length, but all three axes are at right angles to one another.

III. *Monoclinic:* All three axes are of unequal length, and only two are at right angles to one another.

IV. *Rhombic:* All three axes are of unequal length, but all are at right angles to one another.

V. *Triclinic:* All three axes are unequal, and oblique.

VI. *Hexagonal:* There are three axes in a plane intersecting at angles of 60 deg., and a fourth axis through the intersection, perpendicular to the plane.

The three groups of the foregoing classification that hold interest for us are the cubic, the tetragonal, and the hexagonal. Fortunately—for purposes of study—most of the important metals belong to the simplest of these, *i.e.*, the cubic, only a few metals, as zinc, magnesium, and cadmium, belong to the hexagonal, and only one industrial metal, tin, belongs to the tetragonal.

The cubic system, defined by the possession of three equilength axes at right angles to one another, actually permits of two external forms, the simple cube, a six-sided figure, and the octahedron, an eight-sided figure (see Figs. 4 and 5). In this system,

[1] A seventh (trigonal or rhombohedral) type is sometimes included, but is now more generally considered a subtype under the hexagonal.

the "structural unit" may be thought of as a cube, the unit cube, so-called, the simplest case being one with eight atoms, one at each of its eight corners, as shown in Fig. 9a. The indefinite repetition of this structural unit in space gives us the space lattice of the crystal. A photograph of a crystal model of rock salt (sodium chloride), showing the uniformly spaced arrangement of the constituent atoms according to a simple cubic pattern, is shown in Figs. 6 and 7. A careful examination of the solid model, made at various positions relative to the observer, would disclose several interesting facts concerning the relationships of the symmetrically arranged atoms that are less easily ascertained by looking at the photographs. In the first place, one discovers that there are three principal directions, or planes, in which the atoms arrange themselves. These are (1) parallel to the cube faces, as in Fig. 6, or *a* of Fig. 8; (2) parallel
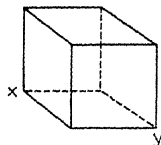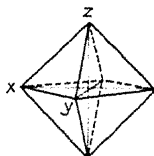
Fig. 4.—A cube.   Fig. 5.— An octahedron

to the face diagonal of the cube, as in Fig. 7, or *b* of Fig. 8; and (3) parallel to the cube diagonal, the *c* of Fig. 8. In the first case, the atomic planes cut one axis (the *x* axis), and are parallel to the other two axes, (see *a* of Fig. 8). For reasons of simplicity, let us think of one cube unit alone, and we shall suppose that the plane intercepts the *x* axis a unit distance from the origin (see Fig. 8). The intercept on the *x* axis is thus unity, whereas the plane, being parallel to the other two axes, intercepts each of them at infinite distance (case *a* of Fig. 8). The intercepts of this family of planes becomes then 1 for the *x* axis and ∞ for the other two axes. However, the notation used by crystallographers to describe planes in terms of the axes of reference employs the reciprocals of the intercepts (the Miller indices, so-called), and not the intercepts themselves. For the family of planes in question the indices are 1, 0, and 0, for the *x*, *y*, and *z* axes, respectively. The particular plane, and the family of planes to which it belongs, are designated the (100) and the {100} planes respectively.
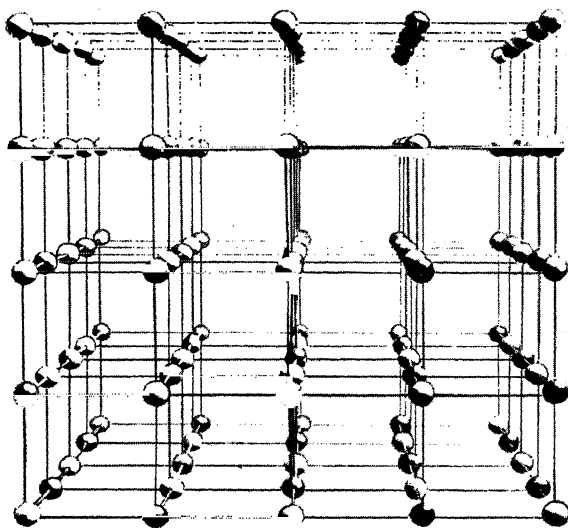
Fig. 6.—Photograph of crystal model, illustrating a simple cubic lattice structure. (Sodium chloride lattice type.)
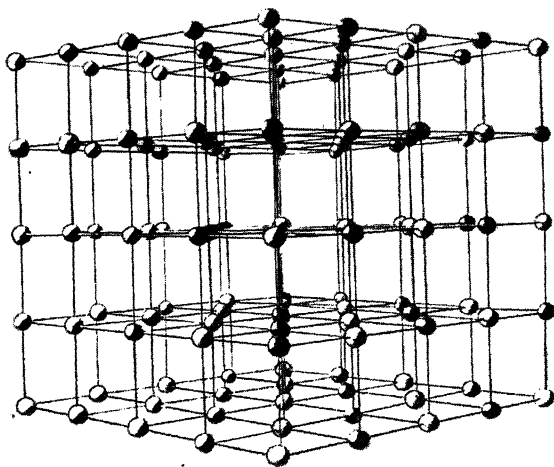

Fig. 7.—Another view of the crystal model of a simple cubic lattice. "Looking down" the {110} family of planes. Note the relationship between the cubic and the hexagonal lattice types that is shown in this view of the model.

In a like manner of reasoning, the plane parallel to the face diagonal is designated the (110) plane, since its axial intercepts are unity on the *x* and *y* axes, and infinity on the *z* axis. Also, the planes parallel to the cube diagonal become the {111} family of planes, since the intercepts on all axes are at unit distance from the origin.
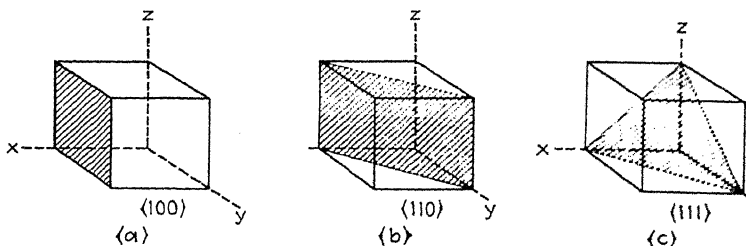
Fig. 8.—Notation of atomic planes.

Another observation that one makes from study of the solid model is that the interplanar distances of these three families of planes differ. The distance between the {100} planes is necessarily unity, since it corresponds to the length (parameter) of the edge of the unit cube. From the geometry of the cube, it is further evident[1] that the distance between the {110} planes is $1/\sqrt{2}$, and that between the {111} planes it is $1/\sqrt{3}$. This matter of interplanar distance is of considerable importance in the physics of metal crystals. Reference will be made to it on another occasion.

A third discovery regarding atom relationships in the solid model is that the number of atoms per unit area (the so-called density of atomic population) differs with the plane family. One finds that the density of population is greatest in that family which has the greatest interplanar distance. One finds also that the three families of planes mentioned do not exhaust the possibilities, indeed that even these may possess somewhat different designations. For example, there are three planes of the cube that bear the generic {100} label, the 100, the 010, and the 001; there are six 110 planes, and eight 111 planes per unit cube.

[1] More simply, by substitution in the formula, $d = \dfrac{a}{\sqrt{h^2 + k^2 + l^2}}$ where *a* is the length of the cube edge; *h*, *k*, and *l* are the intercepts on *x*, *y*, and *z*.

And, finally, one notes that while each cube unit has ostensibly eight atoms, actually each one of these atoms is shared with seven other abutting cubes so that, in reality, an individual unit can lay claim only to one-eighth of each atom, or one atom in all.

This really simple kind of cubic lattice is, however, not assumed by any of the cubic metals. The metal "cube" is of a somewhat more intricate design; in fact, there are two types of cubic structure found among the metals, both of which depart somewhat from the simple cube as described above. The one of these is a nine-atom unit cube, with one atom at the corners of the cube, as in the simple case, and a ninth atom at the geometrical center of the cube. This particular type of cubic architecture is known as the *body-centered cubic* and is illustrated in *b* of Fig. 9. The

(a)
Simple Cubic

(b)
Body-Centered
Cubic

(c)
Face-Centered
Cubic
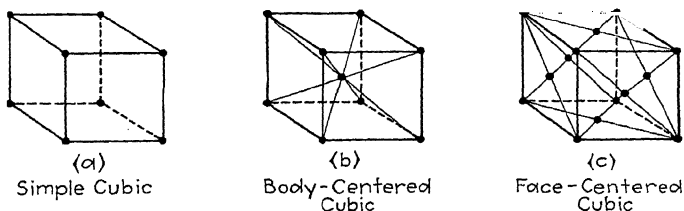
Fig. 9.—Types of cubic lattices.

ordinary form of iron, the low-temperature modification, or alpha iron, and most of the brittle, high-melting point metals (see Fig. 2) are body-centered cubic.

In the body-centered cube, the corner atoms are, of course, shared with neighboring cubes, the center atom is not shared; thus, there are two atoms that belong exclusively to each individual cube unit. Of interest also is the fact that the center atom is included on the (110) and the (111) planes, but not the (100) plane.

The second type of the modified simple cube as found in the metals has 14 atoms per unit cell distributed as follows: one, as before, at each of the eight corners of the cube, and one at the center of each of the six faces. This particular arrangement constitutes the *face-centered cubic* lattice, shown in *c* of Fig. 9. Most of our important industrial metals—the really ductile metals—possess this type of lattice; copper, lead, aluminum, and the noble metals are examples. Iron, between 900° and 1410°C., is another. The six face atoms are shared by the six abutting

cubes, one-half atom to each cube. This gives three face atoms, and (8 × ⅛) one corner atom, or four in all, per unit cube.

Besides the particular type of cubic spacing, one other element is needed to describe fully the lattice characteristics of a metal (or any) crystal, *viz.*, the length of the cube edge, or the distance between the corner atoms. This distance is called the lattice *parameter* and can be readily measured by X ray diffraction methods, specifically by determining the interplanar distance of the {100} family of planes. The parameter (the a of the crystal physicist, expressed in Ångström units, or Å.[1]) of the more common metals is given in Table 1.

TABLE 1.—LATTICE STRUCTURE AND CONSTANTS OF SOME METALS

Metal	Lattice structure	Parameter, Å.	Axial ratio
Copper	Face-centered cubic	3.60	
α-Iron	Body-centered		
γ-Iron	Face-centered cubic		
Lead	Face-centered cubic	4.94	
Gold	Face-centered cubic	4.08	
Silver	Face-centered cubic	4.08	
Nickel	Face-centered cubic	3.54	
Zinc	Hexagonal	2.67	2.67
Tin	Body-centered tetragonal	5.82	1.82
		3.17	

Tin has been cited as the sole example of a common metal which, at ordinary temperatures, exists with a tetragonal lattice; to be more exact tin has a body-centered tetragonal lattice. A tetragonal lattice may most simply be considered a cubic lattice that has been elongated (or compressed) along one axial direction. Thus, two dimensions are necessary to describe the lattice dimensional attributes fully. The length of the two equal dimensions is designated by the usual a, that of the unequal one by c. The axial ratio, c/a, has considerable crystallographic significance. A sketch of the body-centered tetragonal lattice is given in a of Fig. 10.

The third crystal system of metallographic interest is the hexagonal system shown in b of Fig. 10; this system consists, as

[1] An Ångström = 10^{-8} cm.

we remember, of three equal axes in a plane 60 deg. to one another, and a fourth axis at right angles to this plane at the tri-axial intersection. The fourth axis may, or may not, be of the same length as the axes of the triplicate set. The length of the basal axes is designated by the letter *a*, and the fourth axis by
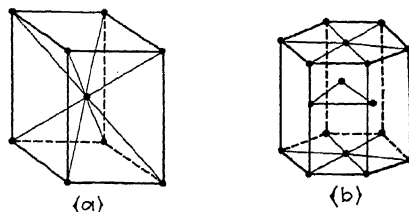

⟨a⟩   ⟨b⟩

Fig. 10.—(*a*) Body-centered tetragonal lattice, and (*b*) close-packed hexagonal lattice.

Fig. 10c.   Fig. 10d.

Fig. 10c.—Diffraction pattern of polycrystalline copper.
Fig. 10d.—Diffraction pattern of a single crystal of copper. (*Photo by Greninger.*)
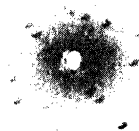
Fig. 10e.—Diffraction pattern of the very pure iron whose photomicrograph is given in Fig. 39a. This photogram was made with the apparatus shown in Fig. 10f. (*Photograph by Eppelsheimer.*)

the letter *c*; as in the tetragonal system, the axial ratio has important crystallographic significance. The fundamental lattice of zinc is hexagonal, but it is of a special type. As a reference to Fig. 10b shows, the unit hexagonal prism may be divided into six equal triangular prisms. The specific lattice of zinc (and of other of the hexagonal metals) has an atom at each triangular prism corner and also one at alternate prism centers. This particular type of

lattice is known as the hexagonal close-packed, and with the face-centered cubic with which it is closely allied, this method of arrangement of the atoms shares the distinction of closest packing of the atoms.

As stated earlier (page 4), the atomic "strata" in a crystal are of the proper interplanar distance to cause the crystal to act as a diffraction grating for radiation of wave lengths corresponding to those possessed by the X rays. One kind of diffraction
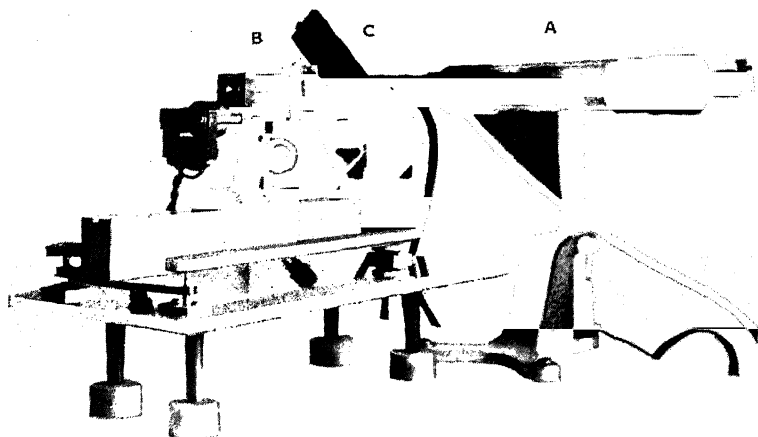

Fig. 10*f*.—Shearer X ray tube, and Sachs back-reflection camera. The film of Fig. 10*e* was taken on this apparatus. *A*, X ray tube; *B*, specimen holder; *C*, film holder. (*Harvard Graduate School of Engineering.*)

pattern (the Laue or pinhole pattern) made by the "reflection" of an X ray beam from the atomic planes of copper is shown in Figs. 10*c* and 10*d*. Other similar photographs are given in Chap. VII. Another type of X ray diffraction photograph is given in Fig. 10*e*, while the apparatus responsible is that shown in Fig. 10*f*.

The lattice characteristics of metal crystals are affected by alloying (see Figs. 47 and 48), by deformation, and by other treatments. Of these various effects, something will be said from time to time, as occasion arises. Suffice it to mention now what has earlier been intimated, *viz.*, that apparently the type of lattice

is of some moment in determining the plastic properties of a crystal, for a reference to Fig. 2 will reveal that the most ductile metals are, in general, those possessing a face-centered cubic lattice. This particular variety of cubic architecture is, seemingly, the one which, under stress, permits of most plastic flow before rupture.

Polymorphism (Allotropy).—Some of the chemical elements, including at least two metals (iron and tin), can exist in more than one crystalline form; this property is called polymorphy, or allotropy. The temperature determines which of two or more polymorphs of an allotropic element shall stably exist. Over one range of temperature, one crystallographic form of the element is stable. At higher or lower temperatures, another form becomes the stable phase. With the changes in crystal form and lattice come changes in properties. The different allotropic forms of iron are given in Table 2. Included also are some of the principal properties of the various modifications. The polymorphism of iron is of the greatest technical importance, for the structure of many steels and the modification of that structure by heat-treatment depend on the fact that iron can exist in more than one form of differing properties.

TABLE 2.—THE ALLOTROPIC MODIFICATIONS OF IRON AND THEIR PROPERTIES

Name	Stable temperature range, °C.	Lattice type	Magnetic properties	Carbon solubility, per cent
α-Iron.....	Up to 904	B.C.C.	Ferromagnetic up to 778°C; paramagnetic above 778°C.	Max. sol. about 0.03
γ-Iron.....	904–1410	F.C.C.	Paramagnetic.	Max. sol. 1.7
δ-Iron.....	1410 to melting point	B.C.C.	Paramagnetic.	Max. sol. about 0.38

The temperature and the velocity of allotropic transformations are, in many cases, considerably influenced by the presence of a second element; the effect of alloying on the temperature of the allotropic change will be discussed in Chap. IV.

Polymorphic changes are, of course, phase changes; they are comparable to the liquid ⇌ solid change occurring at the melting point. There is the usual energy change which is revealed as an

irregularity or "break" in the otherwise smoothly contoured cooling (or heating) curve. However, the energy change involved in allotropy is commonly of somewhat less magnitude than that occurring at the melting point, but it is in the same direction. As one might expect from the rigidity of the solid metal, phase changes in the solid state are more sluggish than those taking place at the melting point. Hence, undercooling and hysteresis effects, producing meta-stable structures, are common concomitants of phase changes in the solid state.

Mechanical Properties.—We now turn to a group of properties which make their possessors—the metals and their alloys—the most important class, by far, of all engineering materials. Since the industrially important mechanical properties are, in general, better developed in the alloys, the more comprehensive treatment of these properties is found in a later chapter. Here we shall limit ourselves to a half dozen or so of the more serviceable metallic properties such as hardness, malleability and ductility, density, etc. Of each of these, some mention has already been made, and each has been defined.

Strength.—One may fairly presume that strength is the most useful engineering property of the metals. The term itself is a comprehensive one and usually requires a limiting adjective to insure a specific meaning. Obviously, tensile strength, compressive strength, torsional strength, etc., are included within the meaning of the term, but one could also, with propriety, designate the elastic limit, the yield-point strength, and hardness as strength properties. They are such, essentially and practically.

The strength of a polycrystalline metal originates tripartitely, —it is, in part, an atomic, a structural, and a granular effect. Accordingly, the strength of a metal is partly intrinsic but is influenced, to a greater or lesser degree, by the metallographic structure of the metal, i.e., by the size and shape of the constituent crystalline grains, by the physical condition (whether cast, annealed, cold-worked, etc.), by the temperature, and by the presence of impurities inadvertently present or purposely added. A typical effect of cold deformation on strength is shown in Fig. 11, that of temperature in Fig. 12, and that of the presence of a second metal in Fig. 13.

Hardness.—The hardness of the common metals varies considerably, but none is very hard as measured by the standard

set by some of their alloys. Where extreme hardness is a requisite property, it is an alloy and not a particular metal that
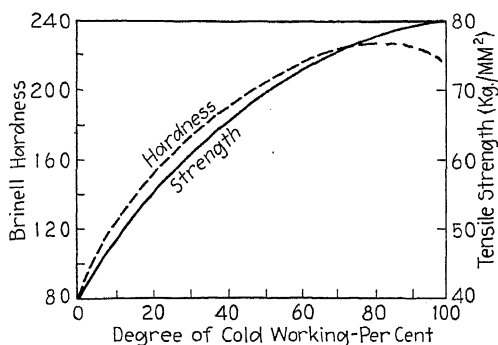

FIG. 11.—Effect of cold deformation (rolling) on the hardness and tensile strength of a pure metal (nickel).
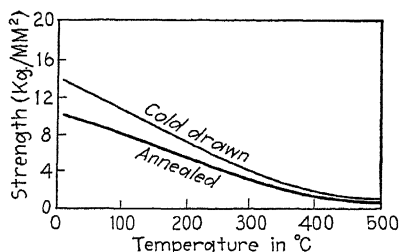

FIG. 12.—Effect of temperature on the strength of cold-worked and annealed aluminum metal.
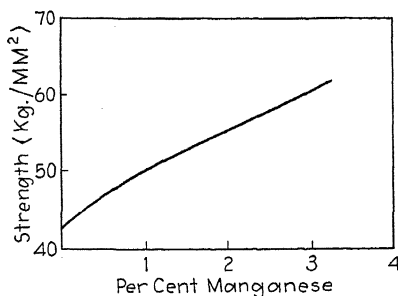

FIG. 13.—Effect of alloying on the strength of a metal; the addition of small amounts of manganese to pure nickel.

is used. There are a number of methods employed to determine relative metallic hardness. The one most widely used is the

"resistance-to-penetration method." Most simply, this method is to cause, by a definite loading, an extremely hard body, of given size and shape, to penetrate the metal whose hardness is to be evaluated; then to measure the diameter or depth of the impression. Plastic flow is obviously involved in this test, so that the determination of the hardness of the really brittle metals is beset with some difficulties, since it produces results of some uncertainty.

Hardness, like its coproperty, strength, is considerably affected by the grain size, by cold deformation, by the presence of impurities (see Fig. 11). It is, perhaps, the mechanical property most subject to change by man's device; certainly in the steels, and only to a lesser degree in other age-hardenable alloys, it is the one most amenable to heat-treatment.

The hardness property has various implications; for example, hard metals and alloys—in common with hard nonmetallics—possess a high resistance to abrasion. This is, in reality, another aspect of the hardness property—scratch hardness. Such metals, in an alloyed condition usually, find use in machine parts (cams, gears, etc.) that move in juxtaposition with like mechanisms, and in countless other devices and appliances in the use of which wear resistance is an important consideration.

Hard substances have ordinarily low coefficients of friction. This explains why most bearing (antifriction) alloys possess one or more hard constituents, usually distributed through a softer, plastic matrix.

Ductility, Malleability, Toughness.—These three related plastic-strength properties are shared unequally by the so-called ductile metals. In Table 3 are given 10 of these metals arranged in order of decreasing ductility and malleability.

Examination of Table 3 reveals the following:

a. Gold and silver are the most malleable and ductile of all metals. (Gold, the more malleable, can be hammered into leaf of 0.0000033 in. in thickness; silver can be hammered into sheet of 0.0001 in. in thickness).

b. Of the ten metals, seven are face-centered cubic; tin, alone, is tetragonal; only zinc is hexagonal and only iron is body-centered cubic. The four most ductile and the three most malleable metals are all face-centered cubic.

c. Tin is fifth and lead seventh in the order of malleability, whereas they drop to the ninth and tenth place in the ductility column. Both are plastic enough, but neither is especially tenacious, so not particularly ductile.

d. Iron is ninth in order of malleability, indicating a not particularly high plasticity of its body-centered cubic lattice. It is in fourth position in the

ductility column, which would tend to show that high tensile strength is an important factor in the ductility property.

TABLE 3

No.	Malleability	Ductility
1	Gold	Gold
2	Silver	Silver
3	Copper	Platinum
4	Aluminum	Iron
5	Tin	Nickel
6	Platinum	Copper
7	Lead	Aluminum
8	Zinc	Zinc
9	Iron	Tin
10	Nickel	Lead

Malleability and ductility are affected by changes in chemical composition; in general, impurities impair this property though not always. Impairment is especially marked if the injurious element is itself brittle and tends to locate in the intercrystalline areas (grain boundaries) of the metal. Probably the best example of this type of intercrystalline brittleness is shown by copper containing very small amounts of the very brittle metalloid, bismuth. This element, because it is practically insoluble in solid copper (though soluble enough in liquid copper) precipitates on solidification, and the precipitated metalloid forms thin films around the copper grains. This network destroys the continuity of the matrix, and makes the metal, as a whole, exceedingly brittle; this is true despite the fact that the individual units of the complex—the copper crystalline grains—are very ductile and tough. The deleterious effect on the ductility of copper of really extremely small quantities of bismuth becomes apparent when one finds, as one authority (Hofman) reports, that 0.00005 per cent bismuth makes copper unfit for wire drawing.

Malleability (and ductility), in most instances, is affected by temperature. Generally plasticity increases with temperature, while the strength drops off. At elevated temperature, rupture occurs usually through want of coherence and not because of any lack of plasticity. All metals will imperceptibly "flow," even

under moderate loads, at sufficiently high temperatures. This is what is called "creep," and creep resistance is an increasingly important engineering property of metals and alloys.

Most metals (*e.g.*, zinc) have temperature ranges in which they become relatively nonmalleable, *i.e.*, they are "short." If the nonmalleable range is around ordinary temperatures, the metal is said to be "cold-short." If at elevated temperatures, it is "hot-short."

Toughness is a property allied to ductility and malleability, and like them it is not a simple property but one with plasticity and strength components. Toughness is the antithesis of brittleness. Tough metals possess the property of resisting impact or sudden shock; *i.e.*, they have the ability to distribute and equalize instantaneously the strain induced by a suddenly applied load. The brittle metals (*e.g.*, antimony) lack this capacity, and a sudden impact causes them to shatter.

Temperature has some effect on toughness; at very low temperatures—*e.g.*, that of liquid air—most tough metals become brittle. But at other temperatures, also, toughness may be reduced to a very low value. Copper just under its melting point and "pure" iron at temperatures around 200° to 250°C. (blue-heat brittleness) are examples of brittleness in otherwise tough metals.

Cold deformation of most metals has an embrittling effect,[1] and in any fabrication process involving considerable working of the metal, periodic annealing is required to restore the normal toughness lest the metal rupture with further deformation.

Density.—The density—mass per unit volume—of the metals is usually high; at least, this is the case for the common metals. Of all metals, lithium has the lowest density and osmium the highest. The densities of some of the more important metals, and—as a matter of interest—those of lithium and osmium, are given in Table 4.

The density of a metal is influenced somewhat by the presence of a second element, but unless there is considerable difference in the densities of the two, the effect is small, at least until relatively large amounts of the second element or metal are present. The effect of alloying on density is not always an

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[1] There is no cold-working effect if the temperature of recrystallization is close to room temperatures.

additive quantity but may be greater than that called for by the simple rule of mixtures. The effect of alloying on density is, of course, of most practical interest in the case of the light-metal alloys, as the aluminum alloys.

TABLE 4

	Density, gm. per cubic centimeter
Lithium	0.534
Osmium	22.48
Magnesium	1.74
Beryllium	1.85
Aluminum	2.70
Zinc	7.14
Tin	7.30
Iron	7.88
Nickel	8.90
Copper	8.93
Silver	10.53
Lead	11.34
Gold	19.32

Cold working also changes (decreases) the density slightly.

The density of all the metals, save bismuth, is less in the liquid than in the solid state. Hence, metals are more voluminous in the liquid than in the solid condition, and shrinkage occurs on solidification. This decreased volume change on freezing has many practical implications. For example, it is the cause of shrinkage cavities, or "pipes" in ingots; it has to be taken into account in the design of molds in foundry work; and in many cases, as in type founding where sharp impressions are necessary, the choice of an alloy will, in part, be determined by its shrinkage characteristics.

Corrodibility.—The metals occur in nature uncommonly as native metals, most often as definite chemical combinations with other elements. These naturally occurring compounds (minerals) are, for the most part, oxides, sulphides, carbonates, hydrated compounds, etc., or in short, associations with those elements whose occurrence is most common and whose active participation in mineral genesis is most general. The meaning of this is clear enough—the metals are chemically active substances, *i.e.*, they may be readily oxidized, sulphurized, or otherwise acted upon by most of the common nonmetallic elements.

One could hardly expect, then, that a metal reduced from one of these compounds would be wholly indifferent if subsequently exposed, under favorable conditions, to the same natural agencies as, for example, air containing, in addition to its own active oxygen, such extraneous gases as carbon dioxide, water vapor, and sulphur gases.

The chemical attack on the metals by natural or artificial corrodents is known generally as corrosion, with specific instances of the phenomenon having such names as rusting and tarnishing. If we accept the electrolytic theory of corrosion as substantially the correct explanation of the phenomenon, we would expect, on theoretical grounds alone, that a pure metal would be more corrosion-resistant than an impure one, for local differences in chemical composition, however small, might instigate galvanic action.   And in particular cases, and under certain conditions, this seems to be true.   But whether the conclusion holds generally one cannot be so certain, for it cannot be experimentally proved as we still lack really chemically pure metals.

With respect to corrosion, the noble metals—gold, the platinum metals, and to a less degree, silver—are in a class by themselves. They are comparatively chemically inert to all common corrodents; only silver is appreciably attacked by sulphur gases. Of the industrial metals, nickel, tin, and chromium, perhaps, show best all-round corrosion-resistant properties.

Besides the natural, inherent susceptibility of the metal to chemical attack, the nature and character of the corrosion product often determine the extent and rate of the attack. Whether or not this product is soluble in the corroding medium, whether it forms an adherent film over the metal surface, or clings loosely thereto, and its relationship, electrochemically, to the metal—all are factors of some consequence in the corrosion process.   Moreover, changes (in composition, temperature) in the corrodent, occurring with time, may alter the character, and thus the duration, of the attack.   Corrosion is, thus, no simple process; so many variables are concerned in most corrosion systems that it is next to impossible to anticipate, except under definite and specified conditions, the corrosion behavior of a metal when exposed to a certain corrodent.

Alloys—*i.e.,* those "impure" metals whose departure from purity is purposeful and considerable—may, or may not, be

more corrosion-resistant than the major constituent metal. In certain alloys, the age-hardening alloys, for example, a finely dispersed phase exists throughout the matrix. This structural complex, because of its very heterogeneity, is especially conducive to corrosion. Also, in some of these and in other alloys, the separating phase tends to segregate locally in grain-boundary areas. This particular kind of segregation gives rise, in many instances, to a peculiarly pernicious form of local attack, the so-called *intercrystalline type of corrosion.*

On the other hand, there are alloys—as, for example, the "stainless steels"—which possess superior noncorrosion properties. Their extraordinary corrosion resistance is usually explained on the assumption that, at the outset of the attack, they form a thin but resistant, highly impervious, and self-perpetuating film which protects the metal surface from further attack.

Corrodibility is affected by temperature, for corrosive attack, like other chemical reactions, is more active and energetic at the higher temperatures. Deformation also increases the susceptibility to corrosion. In a metal where local deformation has occurred or where, with general deformation, a strain gradient exists, the strained areas are usually anodic to the less strained ones. Corrosion is usually accelerated by such circumstances.

Many metallic alloys are, under certain conditions, susceptible to particular and unusual forms of corrosion. For example, corrosion may attack preferentially one constituent of a duplex alloy, leaving the other practically intact. Such an attack leaves the alloy more or less "honeycombed" and, of course, worthless. Again, the insidious "season-cracking" prevalent in other alloys is another form of corrosion.

Destruction and injury of metal structures and vessels by one or more of the various forms of corrosion constitute one of the world's most serious economic losses, running into unknown millions of dollars yearly. It is the result, in no small measure, of the circumstance that iron, the most important metal, is, at the same time, one of the most easily corrodible. There is, however, one very, very small item on the other side of the ledger. Some of the tarnishes—the patinas—have some decorative and aesthetic value. This is particularly true of copper and some of its alloys. This metal and many of its alloyed forms weather in

a beautiful manner. They become covered with a corrosion product (patina or stain) which is not only highly protective but which, with its suggestion of mellow age, distinctly enhances the natural beauty of the original metal surface.

Electrical and Thermal Conductivities.—The specific resistances of some of the principal metals are given in Table 5. Included also, for comparison purposes, are those of two of the border-line metals, antimony and silicon. Evidently, with

TABLE 5.—THE SPECIFIC RESISTANCE W, IN OHM-CENTIMETERS, AT 20°C., AND THE TEMPERATURE COEFFICIENT OF RESISTANCE

$$\left[\frac{1}{W_0} \cdot \frac{W_{100} - W_0}{100} \right],$$

BETWEEN 0 AND 100°C. OF SOME OF THE MORE COMMON METALS
(After Hume-Rothery)[1]

Metal	Specific resistance	Temperature coefficient of resistance
Copper	1.69×10^{-6}	429×10
Silver	1.62×10^{-6}	410×10
Gold	2.4×10^{-6}	400×10
Aluminum	2.62×10^{-6}	467×10
Iron	10.0×10^{-6}	657×10
Nickel	6.9×10^{-6}	634×10
Zinc	6.0×10^{-6}	416×10
Antimony	39.0×10^{-6}	511×10
Silicon	85.0×10^{-6}	*

*See p. 42.

respect to this property, silver and copper are metals quite alone.[2] For economic reasons, copper is, of course, the metal that is used for commercial conduction purposes. Indeed, about one-half of all copper produced is used by the electrical industry, principally in the form of wire. Aluminum, too, has been used in recent years for this same purpose. On a *weight* basis, aluminum is actually superior to copper as a conductor. An interesting comparison of the conductivities of these two metals is given in Table 6.

[1] From W. Hume-Rothery's "The Metallic State," Oxford University Press, by permission of the publishers.

[2] The honor of highest *atomic* conductivity $(C N)$ is, however, shared with the monovalent (alkali) metals.

TABLE 6.—THE RESISTIVITY OF COPPER VERSUS THAT OF ALUMINUM
For hard-drawn conductors of equal resistance

Ratios	Aluminum	Copper
Ratio of diameter...............	1.28	1.00
Ratio of cross section...........	1.64	1.00
Ratio of weight.................	0.50	1.00

The conductivity of a metal is affected by the chemical com-
position, *i.e.*, by the presence of impurities; by its physical condi-
tion (as cold-worked, annealed,
etc.), by the temperature,
and (little) by pressure. The
magnitude of the composition
effect depends largely on the
precise manner of alloying. If
the added metal (or impurity)
is soluble in the principal metal,
the impairment in conductivity
is much more marked than if
the two form a simple mixture.
In Fig. 14a are shown the effects
of some impurities on the con-
ductivity of copper and the
difference in alloying state on
conductivity is evident, (*e.g.*,
oxygen is practically insoluble
in solid copper, and its delete-
rious effect on conductivity is
small compared with that of

FIG. 14a.—Effect of impurities on the
conductivity of copper. (*After Addicks.*)

the soluble phosphorus, arsenic, aluminum, etc.).

The effect of temperature is generally to increase the electrical
resistance. The change in resistance per degree change in tem-
perature is called the *temperature coefficient of resistance.* The
metals, as a rule, have a higher value for this property than do
many of their alloys. Indeed, in some solid solution alloys, the
temperature coefficient is so low as to insure for these alloys
(within temperature limits) a resistance which is quite inde-
pendent of temperature. The temperature coefficients of resist-
ance of a few common metals are given in Table 5. If the

specific resistance were exactly proportional to the absolute temperature, the value of $\left(\dfrac{1}{W_0} \cdot \dfrac{W_{100} - W_0}{100}\right)$ would be $\frac{1}{2}73$, or about 0.0037, but the experimentally determined values are nearly always larger than this as the data in Table 5 show. Some of the metals (of Groups IV, V, and VI) behave abnormally as regards temperature coefficient; for example, they may show a

FIG. 14b.—Microstructure of a typical solid solution alloy. The alpha solution of zinc in copper, containing 30 per cent zinc. (*Photograph by Reed.*)

negative coefficient over one temperature range, and a normal positive one over another (higher) range. Silicon is one of such, titanium is another.

The effect of stress on electrical conductivity, if the resulting strain is within the elastic range, is to decrease slightly the conductivity in the direction of the applied stress, and to give variable but always smaller changes in a direction normal to stress direction. When the elastic limit is exceeded and permanent set occurs, an increase in resistance up to about 8 to 10 per cent.

occurs. The normal conductivity of the metal, in the latter instance, is restored by annealing.

At temperatures approaching zero absolute, some of the metals lose practically all of their resistance. This is the curious phenomenon of *supraconductivity.* An electric current started (induced) in a ring of such a metal in its supraconductivity range goes on for months or even years. The temperatures where lead, tin, and tantalum become supraconductors are, respectively, 7.2° abs., 3.75° abs., and 4.5° abs.

As previously indicated, the metals are excellent conductors of heat. The specific thermal conductivity K is the amount of heat which passes across a unit area in unit time under a unit temperature gradient. Silver is commonly taken as the standard with an assigned value of unity for its conductivity. The relative values of K for some of the other metals are shown in Table 7.

TABLE 7.—THE SPECIFIC THERMAL CONDUCTIVITY K, AND THE WIEDEMANN-FRANZ RATIO (Z) FOR SOME OF THE COMMON METALS
(After Hume-Rothery)[1]

Metal	K	$Z(\times 10)$
Silver	1.000	152
Copper	0.926	150
Gold	0.71	160
Aluminum	0.485	136
Iron	0.147	194
Lead	0.083	165
Bismuth	0.02	214

As in electrical conductivity, silver, copper, and gold are the best conductors of heat. Copper (or one of its alloys) is the material of which heat-transfer devices of high efficiency are usually made. One might suspect that some definite relation exists between electrical and thermal conductivity since the metals possessing a high degree of the one commonly possess a high degree of the other. The Wiedemann-Franz ratio (Z of Table 7) states this relationship. This ratio, K/C, or Z, is nearly a constant for the true metals. However, it is not a fundamental quantity since it is not independent of temperature. This fact is due to the circumstance that while the electrical conductivity is influenced by temperature, the thermal conduc-

[1] From W. Hume-Rothery's "The Metallic State," Oxford University Press, by permission of the publishers.

tivity is not.   In other words, there is a temperature coefficient of electrical resistance, but there is no corresponding temperature coefficient of thermal resistance.

The Property of Alloying.—All subsequent chapters will be concerned with one or another aspect of this important physico-chemical property, and in this chapter's concluding section, we shall limit ourselves to one or two general defining statements.

As chemical elements possessing valence, the metals combine chemically with the nonmetals to form definite polar compounds. These compounds are among the most common of substances, as —to mention but one—sodium chloride. ₍But in addition to actual chemical union, the metals possess the property of interfusion, or of alloying, with one another to form metallic admixtures, or alloys, in which the intermetalline intimacy may vary anywhere from the simple contiguous relationship of the components of a mechanical mixture to the truly involved interconnection of a polar compound.₎ Moreover, this well-developed miscegenetic property of the metals is not exercised exclusively with comembers of the group, for the metals can, and frequently do, alloy with certain of the nonmetals.₍ One may, therefore, define an alloy as an association of some intimacy, of two or more metals, or of one or more metals with one or more nonmetals.₎

That the metals do form solid alloys of some structural complexity and intimacy originates in the happy circumstance that the metals all but universally are mutually soluble at temperatures where they are molten and that the close commutual contact that liquid solubility implies profoundly affects the manner of the freezing process and, in turn, determines the actual physicochemical relationships of the metals in, and the physical distribution of the constituents of, the solid alloy.   By reason of the varied physicochemical relationships (solid solution, intermetallic compound, etc.) possible, and because the distribution of the phases is variable, inherently original properties of the parent metals become modified and sometimes altogether new, and quite unexpected ones are created.   The science of metallography, or physical metallurgy, deals with the study of the internal (gross and fine) structure of the solid alloy, with the practical purpose of explaining properties on the basis of structural relationships.

CHAPTER III

THE EQUILIBRIUM DIAGRAM: I. THE LIQUID SOLID CHANGE

Much, if not all, of the purely factual material of the preceding two chapters was, in intent, simply preliminary and preparatory to the principal matter in hand, *viz.*, the discussion of the metallography of the metallic alloys. It seems reasonable to assume, as has been done here, that a fair notion of the essential nature of a metal, and some knowledge of its fundamental properties should precede any study of the constitution and properties of its more complex alloyed forms.

At the outset, because of the obvious advantage of simplicity, we shall confine our discussion to binary alloys, that is to say, to alloys containing two metals only; the matter of ternary alloys will be considered briefly later.

It is true, almost without exception, that when one molten metal is added to another, at least in proportions that are not too large, the two will dissolve completely in each other to form a single melt. This melt has the chemical and physical homogeneity of a true liquid solution which, in fact, it is. But alloys are not used in the molten state. For reasons that are perfectly obvious, serviceable alloys must be solid. It is, therefore, the condition of the component metals in the solid alloyed state that is of practical interest. Since it is not unreasonable to believe that whatever be the precise manner of the freezing process, it will inevitably go a long way toward giving the solid alloy its metallographic character, and in shaping its general and specific properties, one may ask: What happens to the essentially perfect intersolubility of the liquid state when a binary melt is cooled to temperatures where solidification occurs? As a matter of fact, this question permits of a number of possible answers. In the first place, freezing may not alter, in any essential respect, the mutual solubility prevailing in the liquid state; the alloy after solidification would still be a solution—a *solid solution*—which differs, in no whit, from any solution except that it is solid.

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Now, solid comiscibility, in *all* proportions, may result on solidification of binary melts wherein complete reciprocal liquid solubility existed. Whenever this is so—and not infrequently it is—one has a case of complete solid solubility, that is to say, a mutual miscibility in the solid state that ranges from 100 per cent of one metal to 100 per cent of the other. The more usual case, however, is one of partial solid solubility, even where complete liquid solubility may have prevailed; in other words, the metals have a limited solid solubility for one another. Where the actual composition of the alloy exceeds the solubility limit of one solid metal in the other, a new phase or constituent appears on freezing. From this circumstance arises the duplex structure of many alloys.

The second possibility that may occur on the freezing of a homogeneous alloy melt is the practically complete destruction of intersolubility. By such a solidification procedure, one gets an alloy which is nothing more or less than a mechanical mixture of the two pure component metals, though one must hasten to add that it is such a mixture of a rather special type and kind. And finally, we may have definite chemical compounds (intermetallic compounds) forming on freezing, and these, in turn, may act in much the same ways as a metal would, *i.e.*, they may exhibit varying degrees of intersolubility with the pure metals or show no solubility at all.

A further complicating factor of structural metallography is the circumstance that the particular phase forming at the time of solidification, especially if it is a solid solution, cannot be insured of remaining intact till room temperatures are reached. In the case of many solid solutions of limited solubility, there is the commonly occurring decrease in solubility with fall in temperature, with the rejected phase (solute) precipitating as from any supersaturated solution. Also, from one cause or another, a solid phase, which is apparently stable enough at the time, and the temperature of formation may later, at a lower temperature, change completely or in part to an aggregate structure of two phases. Thus, possible changes are not necessarily exhausted when freezing is complete, for more or less revolutionary changes may occur thereafter. Indeed, the fact that these later changes do take place constitutes one of the most important matters with which metallographic science has to deal.

The specific answer to our earlier question—as to many others of like nature that one may ask of any particular alloy system—may perhaps be most readily ascertained by studying the so-called *equilibrium diagram*[1] of the system in question. The simplest form of this equilibrium diagram (for a binary system) is a two-dimensional graph (*i.e.*, temperature vs. composition) which shows for any composition of a series the experimentally determined temperatures, or range of temperatures, at which changes occur, or perhaps more accurately, the particular phases, with their chemical compositions, that coexist *in equilibrium*, at any temperature, including—when this can be ascertained—room temperatures. The several points, lines, and field boundaries of the diagram are determined and located by various experimental methods—thermal analysis, microscopic and X ray examination, electrical conductivity, dilatometric measurements, etc.—but for the general layout of the diagram the first-named method has usually been employed. The other methods supply additional, more specific, or confirmatory information necessary for a full, correctly detailed picture of any series. These methods have proved of especial worth in the study of the changes that take place in the solid state since these are prone to occur in a somewhat less straightforward manner than those incident to freezing.

The number of possible binary alloys is obviously large, even if we limit ourselves to the 30 or so rather common metals, plus a half a dozen alloy-forming nonmetals. Since the specific equilibrium relations existent in a particular series are peculiar to the series, each of the binary systems possible among the common alloying elements has its own distinctive equilibrium diagram. Thus the number of individual equilibrium diagrams is correspondingly large. But, fortunately, one discovers that strict individuality in diagrams is, in many cases, quite superficial, for in many fundamental ways they possess rather striking similarities. This happy circumstance makes the fact of mere numbers less disturbing, for classification of all diagrams, on the basis of certain common features, into a relatively few type diagrams becomes possible.

A logical classification can be made on the basis of the extent of intersolubility at the *beginning* of solidification and that

[1] Also called the phase or constitution diagram.

existing at the *end*. In accordance with that scheme, the binary alloys fall into five principal groups, two of which, however, are further divisible into subgroups, yet giving in all but eight distinct classes or general series of alloys. Each of these eight main or subgroups can be represented by a type equilibrium diagram, a thorough understanding of the fundamentals of which facilitates the interpretation of the commonly more involved and detailed diagrams of actual, flesh-and-blood alloy systems. It may be stated here that perhaps no one thing has contributed more to our knowledge of metallography than have the careful and accurate determination of equilibrium phase reactions of alloy systems, and the recording of these data in equilibrium diagrams, and also that there is nothing quite so important to the beginner in the study of metallography as the ability to get at the full meaning of these diagrams, including the precise significance of each constructional detail, for, unless one does early acquire a certain mastery of the graphic method of approach to the problem of heterogeneous equilibrium as it applies to alloy systems, he can hope to make little satisfactory progress in the science.

On the basis mentioned in the preceding paragraph, the classes of typical binary alloys, with the specific defining character of each, are as follows:[1]

I. Alloys whose two component metals exhibit unlimited intersolubility in both the liquid and solid states.

II. Alloys whose two component metals exhibit unlimited intersolubility in the liquid state, but show a limited intersolubility in the solid state, and the curves of primary solidification intersect at a minimum — the *eutectic* point.

The three subgroups of incomplete solid solubility may be described as showing:

a. No solid intersolubility.

b. A partial solid intersolubility.

c. The formation of actual intermetallic compounds, which are either wholly insoluble in one or both of the two metals, or partially soluble in one or both.

III. Alloys whose two component metals exhibit unlimited intersolubility in the liquid state, a partial solubility in the solid state, and the curves of primary solidification intersect at a transition point which corresponds to the temperature of the *peritectic* reaction.

[1] The author is indebted to Dr. Samuel Hoyt ("Principles of Metallography," Vol. I) for this simple yet inclusive modification of Roozeboom's classification (*Zeitsch. physikal. Chem.*, **30**: 384, 413, 1899).

The two subgroups are determined as to whether the product of this peritectic reaction is

　　a. A solid solution; or

　　b. An intermetallic compound.

IV. Alloys whose two component metals exhibit limited intersolubility in both the liquid and the solid states.

　V. Alloys whose two component metals exhibit no intersolubility in either the liquid or solid state.

The above bare, defining statements of the several alloy groups introduce ideas and terms whose meanings will become clear in the course of the discussion that follows.

Group I. Alloys Whose Two Component Metals Exhibit Unlimited Intersolubility in Both the Liquid and Solid States.—

Composition—Wgt. Per Cent ——→
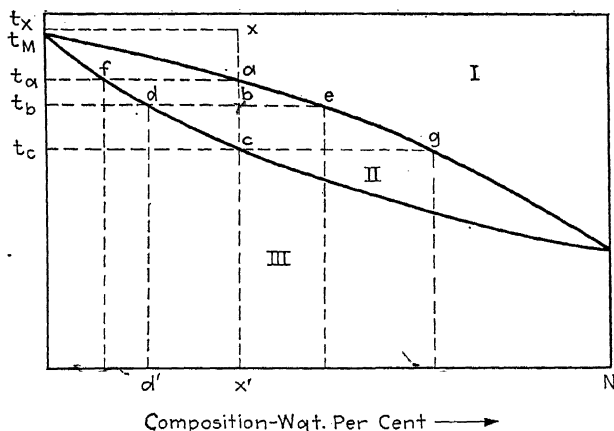
FIG. 15.—Equilibrium diagram of metals M and N, which exhibit unlimited solubility in each other in both the liquid and solid states.

We have here, perhaps, the simplest case, and one that is not infrequent among the binary alloys. Let us restate: We have two metals that are soluble in each other, in all proportions, in both the liquid and solid states. Above the melting point, the two metals form a homogeneous liquid solution, below they form a like solution, but solid, of course. The equilibrium diagram of an alloy of this group is given in Fig. 15.

We shall take a perfectly general case—two metals which we shall call M and N, the former with a melting point of t_M, and the latter with a somewhat lower melting point, t_N. In the

equilibrium diagram (Fig. 15) points along the horizontal axis represent compositions in weight per cent; at the extreme left is 100 per cent of metal M, and of course, 0 per cent of metal N. At the other end of the diagram is 100 per cent of metal N and 0 per cent of M. Distances along the composition axis (MN) give the composition, in per cent of either metal, of any alloy. The vertical axis represents temperature.

The upper curve $(t_M aegt_N)$, connecting the melting points of the two metals, marks the beginning of freezing (or the end of melting) of the alloys of the series. Above it, all alloys are molten, and for this reason it is called the *liquidus*. The lower curve $(t_M fdct_N)$ marks the end of freezing (or the beginning of melting) of the alloys of the series. Below it, all compositions are solid, and it has the name *solidus*. The field included within the liquidus and solidus boundaries (designated II) is a two-phase field, a heterogeneous field. Any alloy within it is partly liquid and partly solid. The field above the liquidus (designated I) and that below the solidus (designated III) are each single-phase fields, alloys in the former consisting of a homogeneous melt and those in the latter (under equilibrium conditions[1]) of a homogeneous solid solution.

From what little has been said, one might infer at least one fundamental difference between the freezing, or melting, of a solid-solution alloy and the similar occurrences in a pure metal. This rather obvious difference is that whereas a metal melts and freezes at a single, definite temperature, an alloy freezes and melts over a range of temperature. In other words, there is no change in temperature of the system while a pure metal freezes (or melts), while in an alloy the temperature continues to drop whilst solidification is going on, or continues to rise when fusion is taking place. An examination of the above equilibrium diagram should make this difference clear. Metal M freezes (or melts) at temperature t_M, a definite *point* on the temperature axis; the same thing holds true for metal N, with its single, definite freezing point t_N. An alloy of composition $(x\text{-}x')$, of somewhat less than 50 per cent of metal N—to take a general case—begins freezing at temperature t_a, and ends at temperature t_c. Freezing, then, takes place over a temperature range of some

[1] It must be remembered that the equilibrium diagram, as the name would indicate, gives a true picture only when equilibrium is attained.

magnitude. This is the case, also, for the reverse process of melting; this begins (for this particular composition) at temperature t_c, and ends at temperature t_a.

The freezing-point curve (cooling curve) of the alloy $(x-x')$ is instructive. In fact it supplies the information necessary to locate the points t_a and t_c. But, first, let us recall the essential features of the freezing-point curve of a pure metal (Fig. 3). This curve consists of three portions—one $(a-b)$ which represents the cooling of the liquid metal to freezing; a second portion $(c-d)$ which represents the cooling of the solid metal to room temperatures; and a third, horizontal portion $(b-c)$ which gives the time interval during which freezing occurs. The freezing-point curve of either of the two metals, M and N, is such a curve, and the temperature of the horizontal portion in each instance locates t_M and t_N, respectively, in the equilibrium diagram (Fig. 15).

The freezing-point curve of the alloy $(x-x')$ is given in Fig. 16. It, too, consists of three parts. The part $(a-b)$ represents the cooling of the melt to the beginning of freezing; $(c-d)$ represents the cooling of the solid alloy to room temperatures; and $(b-c)$ represents the time—and temperature—intervals of freezing. The specific freezing behavior of this alloy is as follows: When the alloy has cooled to temperature t_b (t_a in Fig. 15), freezing begins with the separation of solid crystals; this is an exothermic process. There is, thus, a retardation in the cooling rate of the alloy owing to the latent heat of fusion, and this makes itself felt in the change in slope of the time-temperature curve at b. Quite naturally, the slope becomes less. The slope changes gradually, from b to c, as further separation of solid crystalline matter leaves less and less residual melt to freeze. At c, where solidification is complete, the portion $(b-c)$ passes rather imperceptibly into the again constant-sloped portion of the curve $(c-d)$, representing the now uniform cooling of the solid alloy to room temperatures. We see, then, that the freezing of a pure metal involves a time interval only, whereas in the freezing of a solid-solution alloy, both time and temperature intervals are concerned.

The point b of the freezing-point curve of Fig. 16 becomes point a on the liquidus of the equilibrium diagram (Fig. 15). Both mark the beginning of solidification. Point c of the freez-

ing-point curve becomes c on the solidus of the equilibrium. Both indicate, on the respective curves, the end of the freezing process. If we take an alloy composition somewhat to the left of $(x$-$x')$, *i.e.*, one richer in metal M, we would get a freezing-point curve similar to that just described, as far as type and general contour are concerned, but the temperatures of initial and final freezing would be a little different (somewhat higher in both cases). The same kind of similarity would be true for the freezing-point curve of a composition to the right of $(x$-$x')$; here again, any difference would be limited to the actual temperatures involved. As a matter of fact, no two alloys of the series would be exactly alike with respect to their temperatures of initial and final freezing, but these differences would be con-
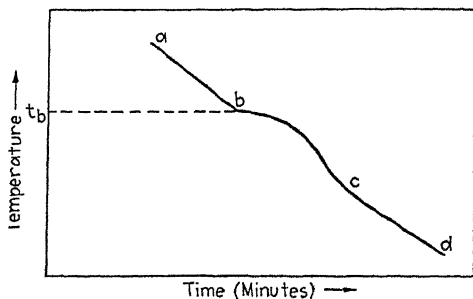
Fig. 16.—Freezing-point curve of alloy of composition $(x$-$x')$

tinuous; the one set of points, those marking the beginning of crystallization, would fall along one continuous curve, the liquidus; and the other set, the final temperature points, would fall along another, the solidus curve.

Thus, an equilibrium diagram is most simply a composite of many (of all) freezing-point curves. It is a temperature-composition graph while the freezing-point curve is a time-temperature curve. We have, then, in an equilibrium diagram, a two-dimensional graph wherein are depicted, in effect, the relations existing between three variables.

In addition to the circumstance that freezing and melting in a solid solution alloy occur over a temperature range, one other patent fact is in evidence with respect to this phase change: One has reference to the fact that the beginnings of melting, *i.e.*, the solidus temperatures, are somewhere between the melting

points of the two constituent metals. The addition of metal N to M lowers the melting points of the resulting alloys, but not to the extent that any alloy has a melting point actually below that of the lower melting-point metal. On the other hand, if one wishes to consider metal N as the solvent metal and metal M as the additive, or solute metal, the effect of alloying is, then, to raise the melting point. There are many cases, as we shall presently see, where the depressing effect on the melting point is a two-sided affair, and the addition of either metal to the other gives an alloy whose melting point is lower than the melting point of either of the metals.

To acquire speedily a working knowledge of the subject, let us inquire a little more fully into the precise manner of the freezing of a typical alloy of this series. We want to know just *how* a melt, a liquid solution, of metals M and N transforms into a solid solution of M and N. For this purpose, we shall again take the general case—the alloy $(x$-$x')$—reference is made again to Fig. 15. We shall start with the alloy at temperature t_x, for at that temperature the alloy is entirely molten, and the two metals are in complete solution in one another. We shall now permit the melt to cool slowly (one insists on cooling *slowly* so as to insure equilibrium always). With fall in temperature, no change occurs till the liquidus is crossed, at temperature t_a. Then the alloy begins to freeze by the separating out of a tiny solid crystal.[1] The chemical composition of that initial crystalline solid is not that of either of the two metals, *i.e.*, it is neither the one pure metal nor the other, nor—what is more surprising—is it exactly that of the liquid alloy. If, in some ingenious way, this early bit of crystalline matter could be removed from the bath and its composition determined, it would be found to contain both metals, but it would be richer in metal M than the parent melt. Its exact composition can be had by physico-chemical methods, in this way: Draw af parallel to the composition axis, through a; and from where af cuts the boundary of the heterogeneous field (the solidus, in this instance), drop a vertical ff' to the composition axis. The composition of the initial separating solid is given by the distance Mf' along the composition axis, *i.e.*, it has a composition of Mf' per cent of metal N,

[1] There are, of course, countless nuclei in the melt which act as centers of crystallization; we shall speak, however, as if there were one.

and Nf' per cent of metal M. Since the composition of the original melt was Mx' per cent of metal N, the new solid phase is poorer in that metal than the melt from which it forms. This particular circumstance is, in reality, a general fact, and it gives us a worth-while rule to remember, *viz.*, the solid phase separating on freezing is always poorer than the melt in that metal that lowers the freezing point.[1]

The separation of the solid phase relatively poor in metal N, obviously, leaves the melt proportionately richer in that metal. As N is the depressant metal, an increased concentration of N in the melt requires a further lowering of the temperature before any more solid will form, or in other words, before freezing can continue. This is, of course, only another way of saying what we already know, *viz.*, that an alloy freezes at an inconstant temperature. It suggests, furthermore, a second rule that one may, with profit, fix in mind: when the solid phase (or phases) forming from a melt has the same composition as that of the melt, freezing occurs at a single, invariable temperature, but if the composition of the precipitating phase differs from that of the parent melt, the temperature of freezing changes (lowers) during solidification.

Assume that the temperature drop slowly somewhat below temperature t_a—let us say—to temperature t_b. The composition of the melt (a gradual enrichment in metal N), in the meantime, moves right along the liquidus from a to c. At temperature t_b, the still molten portion of the partly solidified alloy will have the composition Me' per cent of metal N. The composition of the solid portion of the alloy has meanwhile moved right along the solidus from f to d. At the temperature t_b, the composition of the solid phase *in equilibrium* with the melt of composition Me' per cent of N is Md' per cent of N. Thus it is, during freezing, that the compositions of the residual melt and the solid phase continuously change, or to state the same fact in physico-chemical terms, for any temperature within the hetergeneous field, there is a definite equilibrium composition for each of the two coexisting phases.

With further drop in temperature toward the solidus temperature t_c, the composition of the shrinking residual melt moves farther along the liquidus, and the last bit of melt to freeze has

[1] Not "poorer in the metal of lower melting point," as i

the composition represented by Mg' per cent of metal N. The solid with which this last bit of melt is in equilibrium has the composition Mx' per cent of metal N, for as temperature drops toward the solidus, the composition of the solid phase moves too toward the right along the solidus from d to c. The two extreme limits of composition of the solid solution are, thus, the Mf' per cent of N of the first crystalline matter to form, and the Mg' per cent of N of the final remnant of the liquid to solidify. But under conditions of true equilibrium, as we, all along, have assumed to prevail—which simply means a cooling slow enough to permit the necessary diffusion to take place—the composition of the completely solidified alloy is *exactly* and *uniformly* that of the original melt. That this is not always the case is a fact that need not concern us here.

A summary of the above paragraphs furnishes a third rule. It may be stated as follows: To find the compositions of the phases in equilibrium at a particular temperature, draw a line through the temperature in question parallel to the composition axis, and from where this line intersects the boundaries of the heterogeneous field drop perpendiculars to the composition axis. The distances along this axis from the origin to the intersecting points give the compositions of the two phases.

The components of the three fields of the diagram are:

   I. Melt.
  II. Melt solid solution.
 III. Solid solution.

We shall close this discussion with a statement of the so-called "lever relationship." This rule indicates the relationship between the relative *amounts* of the two phases present at any particular temperature; it does quantitatively what the last stated rule does qualitatively. For the general alloy composition $(x\text{-}x')$, the relative amounts of the two co-existing phases, at temperature t_b, can be expressed as:

$$\frac{W_1}{W_2} = \frac{db}{be}$$

where W_1 and W_2 are the weights of the melt and solid alloy, respectively, and db and be are the lengths of the two "lever-arms" comprising the distance included within the heterogeneous

field, along the line drawn through *b*, parallel to the composition
axis.

**Group II.   Alloys Whose Two Component Metals Exhibit
Unlimited Intersolubility in the Liquid State but Show a Limited
Intersolubility in the Solid State, and the Curves of Primary
Solidification Intersect at a Minimum—the Eutectic Point.**—
This general statement tells us that we are dealing with two
metals that are completely soluble in the liquid state, but are
only incompletely so after solidification.   There is the descriptive
addendum that the liquidus passes through a minimum, the
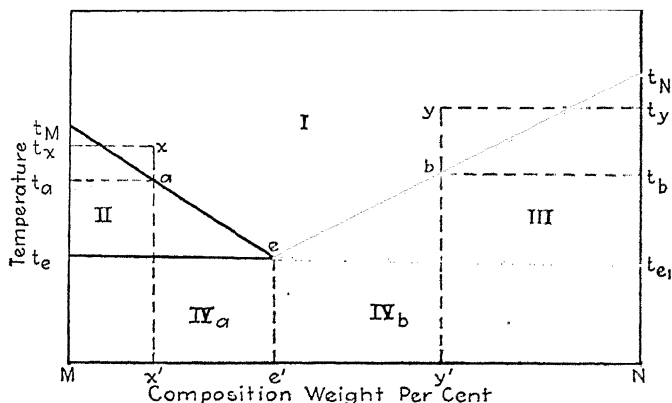
FIG. 17.—Equilibrium diagram of metals *M* and *N*, which exhibit unlimited
liquid solubility and complete solid insolubility.

eutectic point.   This incompleteness in solid solubility may
mean no solubility at all (case *a*), or it may mean, as is more
often the case, that some actual solid solubility exists (case *b*).
Then, again, intermetallic compounds may form on solidification,
and these, in turn, may show some or no solubility in the two
solid metals.   This last possibility accounts for the third case
under Group II.   We have, therefore, not one but three different
diagrams to discuss here.

Case a.   No Solid Intersolubility.[1]—The equilibrium diagram
of this first subgroup is given in Fig. 17.   We shall take, as in the

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[1] On theoretical grounds, objection may be made to this case of the
classification.   It is true that no metal freezes from an alloy melt absolutely
uncontaminated by the other metal (or metals).   There is always some
solid solubility.   But for pedagogical reasons, if for no other, the *type* alloy
should be properly included in the discussion.

previous instance, the two hypothetical metals M (m.p. $= t_M$), and N (m.p. $= t_N$). The liquidus t_M-e-t_N is V-shaped, with the minimum point at e. This point corresponds to Me' per cent of metal N, and to a temperature t_e. The point e is the eutectic[1] point, mention of which has already been made. The alloy of eutectic composition (that is, Me' per cent of metal N, and Ne' per cent of metal M) is the lowest melting-point alloy in the whole series; it is, also, the only alloy in the series—the pure metals excepted—which freezes and melts at a single temperature.

The solidus is the horizontal $t_e e t_{e1}$. Its horizontality indicates that the temperature of the *end* of freezing is quite independent of composition. Not so, however, is the beginning of this phase change, for the addition of either metal to the other lowers the temperature of incipient freezing. All alloy compositions above the liquidus (field I) are liquid, and all below the solidus horizontal (field IV) are solid. In the heterogeneous field—now divided into two parts—solid and melt coexist.

As was done in the case of complete solid solubility, we will follow the progress of solidification of one or more typical compositions. One such is $(x$-$x')$. This alloy contains less of metal N than the eutectic composition. From the point of view of this particular metal, an alloy whose composition lies to the left of the eutectic, as does $(x$-$x')$, is a hypo-eutectic alloy. At the temperature t_x, the alloy is completely molten, for we are above the liquidus. On slowly cooling, no observable change occurs till the liquidus temperature t_a is reached; then solidification begins—the first bit of crystalline matter forms. The chemical composition of this initial solid phase can be determined by applying the rule previously learned, *i.e.*, by drawing line at_a through point a of the liquidus, parallel to the composition axis; and dropping from the point of its intercept with the heterogeneous field boundary (in this case, the vertical temperature axis), a normal to the composition axis. This last line is, of course, the temperature coordinate of the diagram. This gives us, as the composition of the new solid phase, 100 per cent of metal M, and 0 per cent of metal N. In other words, the first-forming crystals are crystals of pure M. Of course, this is what should have been expected, for complete solid insolubility means obviously that

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[1] From the Greek, $\epsilon \hat{v} \tau \eta \kappa \tau o s$; easily melted.

the crystals that separate do so in the pure, uncontaminated condition.

The separation by freezing of pure M leaves the melt proportionately richer in the second metal—metal N, and consequently some slight lowering of the temperature below t_a must precede further freezing, for here, as in the previous alloy, the composition of the separating phase differs from that of the parent melt; thus, the freezing temperature is not a constant quantity. Continued cooling down to the solidus, to temperature t_e, results in further separation of metal M, the composition of the melt moves meanwhile toward the point e, along $t_{M}ae$. At the temperature t_e, the solid phase (metal M) is in equilibrium with the residual melt of eutectic composition (Ne' per cent of M), or from the equilibrium point of view of the relations of the two phases, the melt of eutectic composition is *saturated*, at temperature t_e, with metal M.[1]   Any further lowering of the temperature will result, necessarily, in the crystallization of more solid M. However, we shall leave further consideration of this alloy for a moment—we must remember that it is still only partly frozen—to observe the freezing behavior of a companion alloy, but one whose composition places it to the right of the eutectic composition, a hypereutectic alloy, one relatively rich in metal N.

To this end, we shall take again a general case, *e.g.*, the alloy of $(y-y')$ composition. Cooling from a temperature t_y, where the alloy is completely molten, to the liquidus temperature t_b, the melt will suffer no change. But, as soon as the latter temperature is passed, solidification begins with the freezing out of pure N crystals (crystals of N, and not of M, because we are now dealing with an alloy richer in metal N than is the eutectic composition). As the temperature continues to drop toward the solidus, crystals of N continue to separate out, and the composition of the melt, becoming proportionately richer in metal M, moves along $t_{N}be$. By the time the falling temperature has reached the eutectic temperature t_e, the composition of the residual melt has become of eutectic composition; it now contains Me' per cent of N. The melt of this composition, at this tem-

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[1] The liquidus may be regarded all along as a solubility line. Thus, not only is the eutectic composition saturated with M, but all melt compositions to the left of the eutectic are likewise saturated, but of course, at other (higher) temperatures.

perature, is saturated with metal N, and further lowering of the temperature will result, of necessity, in further crystallization of N. But, from the discussion in the preceding paragraph, we have seen that the melt of this same composition (Me' per cent N and Ne' per cent M), and at this identical temperature, is saturated, also, with metal M; to drop the temperature lower would necessitate the precipitation of this metal. As a matter of fact, further cooling of the alloy of eutectic composition, below temperature t_e, will result in the simultaneous precipitation (or freezing) of both metals. And, this is so regardless of the direction of approach. Whether we start with an M-rich alloy, as is the (x-x') alloy, or one rich in N, as (y-y'), the last stage in the freezing process is the same, *viz.*, the freezing out of the two metals, side by side. Quite to be expected, the metallographic structure developed by this final act of solidification is a distinctive one. It is commonly called the eutectic structure and presents, in its most usual form, a laminated appearance (see Fig. 78).

Let us now review the complete freezing procedure of these two representative alloys. The alloy of composition (x-x') begins freezing at temperature t_a, by the separation of crystals of pure M; as the temperature falls through the heterogeneous field, metal M crystals continue to freeze out. In the meantime, the melt, growing more and more concentrated in metal N, changes in composition along ae. At composition e, and temperature t_e, the melt is saturated with metal M (as, indeed, it has been at all temperatures subsequently), and—because of the enrichment of the melt in N—it is saturated with this metal also. Solidification is completed with the freezing of the two metals simultaneously—with the formation of a eutectic. The completely solid alloy consists of crystals of pure M, and a eutectic mixture of M and N. This eutectic mixture consists of Me' per cent of N, and Ne' per cent of M. (And, indeed, this is the case irrespective of the composition of the original alloy, and whether it is to the right or to the left of the eutectic composition.)

The N-rich alloy, whose typical composition may be taken as (y-y'), begins freezing at t_b. Crystals of pure N freeze out at this temperature, and continue to do so as the temperature drops of t_v. The melt, in the meantime, becomes richer in M, and in composition varies from b to e. At the eutectic com-

position, the melt is saturated with N (as, indeed, it has been at every other temperature from t_b to t_c), but now, for the first time, it is saturated with M also. Freezing is completed with the concurrent deposition of the two metals, forming again the eutectic mixture of the same composition and type as that noted above in the case of the alloy of $(x\text{-}x')$ composition. The now completely solid alloy consists of crystals of pure N, plus a eutectic of M and N.
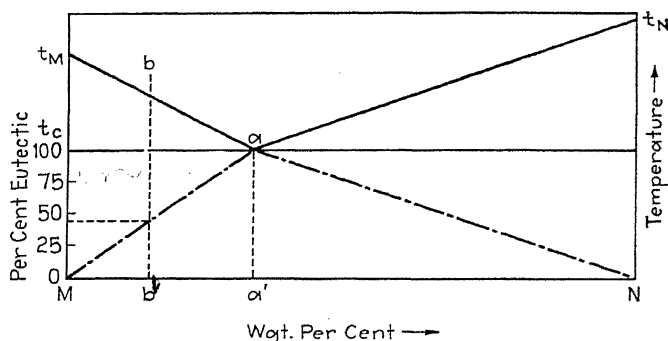
Fig. 18.—Structural composition of an eutectiferous series.

We can now describe the various fields of the diagram, as follows:

    I. Melt.
   II. Melt and solid metal M.
  III. Melt and solid metal N.
 IVa. Solid metal M and eutectic (of M and N).
 IVb. Solid metal N and eutectic (of M and N).

An alloy of exactly eutectic composition (Me' per cent of N, and Ne' per cent of M), would obviously freeze with the formation of 100 per cent eutectic. There would be neither free (proeutectic) M, nor free N present, the microstructure would show only the eutectic constituent. The two extreme compositions of the series—the two pure metals—show, necessarily, no eutectic. It is possible, therefore, to estimate quantitatively the composition of an eutectiferous alloy from its microstructure. An alloy (see Fig. 18) which shows under the microscope a structure which is completely eutectic would obviously be of eutectic composition and would have the composition of Ma' per cent of

N and Na' per cent of M. On the other hand, an alloy which has a microstructure of approximately 40 per cent of eutectic and 60 per cent of metal M would have the composition Mb' per cent of N and Nb' per cent of M.

The melting of an alloy of a eutectiferous series, while quite the reverse of the foregoing, is still an interesting phenomenon. The slow heating of such a solid alloy [let us return to composition $(x\text{-}x')$ of Fig. 17] causes no change till the eutectic temperature t_e is reached; then the eutectic portion of the alloy melts as a unit, and at constant temperature. This portion thus melts much as a pure substance does, *i.e.*, without change in temperature of the system. When the eutectic is completely fused, the temperature rises (with continued heating, of course) with the consequent solution (melting) of pure metal M. This second
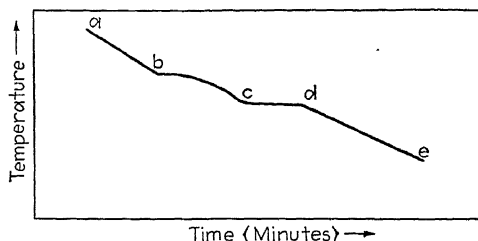
FIG. 19.—Ideal freezing-point curve of a typical alloy of a eutectiferous series.

stage of the melting process continues to the liquidus temperature, to t_a, where fusion is complete. Compositions to the right of the eutectic, those rich in metal N, melt in the same fashion, there is, first, the fusion of the eutectic at constant temperature, followed by the melting of the pro-eutectic N with gradually increasing temperature to the liquidus. The melting of a 100 per cent eutectic alloy exhibits but one stage—a mass melting of the eutectic mixture at a single, constant temperature.

The "two-stage" freezing (or melting) of a eutectiferous alloy, as above described, may be further illustrated by a study of the freezing-point curve of such an alloy. One such (ideal) curve is given in Fig. 19. As is readily evident, the freezing-point curve of this type of alloy shows four parts. The upper portion of the curve $(a\text{-}b)$ represents the normal cooling of the melt to the beginning of freezing. The next lower portion, of somewhat less slope $(b\text{-}c)$ represents the separation (freezing) of the

constituent (metal) in excess of the eutectic composition, as for example, metal M in the alloy $(x\text{-}x')$, of Fig. 17. This separation is, of course, exothermic in its nature, which fact accounts for the change in slope at b. The part $(c\text{-}d)$ represents the freezing of the eutectic, when both metals freeze out (crystallize) concurrently. As the crystallizing eutectic is of the same composition as the parent melt, the portion of the curve which denotes its freezing is horizontal. During its formation, there is an actual halt in the cooling process as the energy released by the exothermic reaction compensates for the energy dissipated. The part $(d\text{-}e)$ represents the cooling of the solid alloy to room temperatures. Its slope is somewhat different from that of the $(a\text{-}b)$ portion, representing the cooling of the melt, since the specific heats of the liquid and the solid states commonly differ.

The nearer in composition the alloy is to the eutectic composition, the larger is the amount of the eutectic relative to the excess metal there is to freeze, and the greater is the magnitude of the accompanying heat change involved in this stage of the freezing process. Thus, the longer will be the horizontal portion of the curve, and the less prominent, relatively, the $(b\text{-}c)$ portion. Also, with varying composition, the beginning of solidification occurs at different temperatures; in other words, the point b varies with composition. This is not so with the temperature of final solidification, for the temperature—if not the length—of the horizontal portion $(c\text{-}d)$ is quite independent of composition.

Case b. A Partial Solid Solubility.—The two foregoing examples of type equilibrium diagrams represent extreme cases of solid solubility among binary alloys. In the one of these—the first example studied, *viz.*, that of type I—we were dealing, as we recall, with a general case of complete solid solubility, where the 100 per cent mutual miscibility of the two metals in the liquid state suffers no appreciable diminution during solidification, the latter process producing a solid alloy wherein the two metals, as before freezing, are soluble in each other in all proportions. In the second case, we had an instance where freezing does effect this liquid intersolubility in a most thoroughgoing and devastating manner, effacing it so completely that there results a solid alloy whose component metals show for each other practically no solubility at all. Naturally, one would expect to find in some alloys degrees of solubility somewhere between these two

extremes; this is, in fact, true, and case *b* is typical of those cases of partial solid solubility. The equilibrium diagram of case *b* of Group II alloys is given in Fig. 20.

Quite plainly, we are meeting with no entirely new diagram for this one resembles, in all its salient features, the diagram of the preceding case. Here as there, is the V-shaped liquidus, with the minimum occurring at the eutectic point. Here is also the horizontal solidus, the locus of the eutectic temperatures, but now extending only part way across the diagram. This failure of the eutectic horizontal to reach to the extreme limits of the
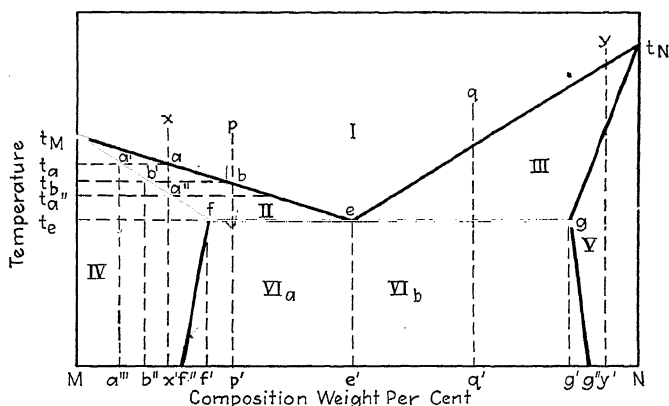
Fig. 20.—Equilibrium diagram of metals *M* and *N*, which exhibit unlimited liquid solubility, and partial solid solubility.

diagram, *i.e.*, to the composition of the two pure metals, differentiates essentially this diagram from that of case *a* and indicates necessarily that here the pro-eutectic phase separating on cooling is not a pure metal as in that instance, but one metal containing in solution some amount of the other. In other words, the initial crystallizing solid is a solid solution of limited solubility. The sloping lines, $(t_M\text{-}f)$ and $(t_N\text{-}g)$, with the eutectic horizontal $(f\text{-}e\text{-}g)$, constitute the solidus of the diagram.

To continue with our previous practice, we shall discuss the cooling procedure of a few representative compositions of the series. First, however, it might be well to put in words the general picture of equilibrium that the diagram gives. This we should be able to do without too much difficulty after our experience with the two preceding cases. We have two metals, *M* and

N, of melting points t_M and t_N, respectively, which dissolve completely in each other in the liquid state but which are only partially soluble in each other in the solid state. The two metals, or more correctly, their two solid solutions, form an eutectic at Me' per cent of N (Ne' per cent of M), melting at temperature t_e. At this temperature, metal M can dissolve Mf' per cent of N, and metal N can dissolve Ng' per cent of M. These two amounts, respectively, represent the maximum equilibrium solubility, at any temperature, of one metal for the other in the solid state. One may ask: What happens when this solubility is exceeded? The answer is that a new phase—the second solid solution—puts in its appearance. The precise manner of its doing this will be seen in a moment when we discuss the cooling of an extra-solubility-range composition as $(p\text{-}p')$. First, however, let us take a composition well within the solid solubility limit, as $(x\text{-}x')$, in the cooling of which there is no such complication. The alloy starts freezing at temperature t_a, the liquidus temperature, and the first crystals deposited have the composition Ma''' per cent of N (dissolved in M). They are, thus, not pure M, but they are richer in M than the parent melt. With continued drop in temperature to $t_{a''}$, the solidus temperature, the composition of the solid moves along the solidus from a' to a''. The alloy is completely solidified at $t_{a''}$ and remains unchanged on further cooling to room temperatures. In truth, this alloy freezes in the same way and with the same results as any alloy of type I. A similar statement could be made with respect to the composition $(y\text{-}y')$, on the other side of the diagram, and no description of its freezing mechanism seems necessary.

The alloy of composition $(p\text{-}p')$, one richer in N than the limiting solid solubility of this metal in M, begins freezing at temperature t_b, with the separation of M-rich solid-solution crystals of Mb'' (per cent of N) composition. As cooling proceeds to temperature t_e, the composition of the solid phase moves, as before along the solidus from b' to f, at which composition (Mf' per cent of N), the solid phase (solution) is saturated with M. The melt has meanwhile varied in composition along the liquidus from b to e. Further cooling of this melt must result in the precipitation of more M in the form of the M-rich solid solution. From what we already know about eutectic systems, we know that the melt of eutectic composition is saturated with the other

solid phase, too, that is to say, with N. Any cooling below t_e, will result in this metal's separation, but because at the eutectic temperature, metal N can dissolve Ng' per cent of M, N does not freeze out as pure N, but as an N-rich solid solution, containing, as a maximum, Ng' per cent of M. So, it happens that when alloy $(p$-$p')$ cools through the eutectic temperature, the eutectic mixture that forms is one consisting of an M-rich solid solution containing Mf' per cent of N, and an N-rich solution containing Ng' per cent of M. For purposes of reference, we shall call the former the alpha solid solution, and the latter the beta solution. The initial state in the solidification of the type alloy $(p$-$p')$ is the freezing of the alpha solution with varying (falling) temperature, and the final stage, occurring at constant temperature, is the concurrent freezing of the saturated[1] alpha and beta solutions, to form an eutectic mixture of invariable composition. The wholly solid alloy consists, then, of crystals of the pro-eutectic alpha solution, and a eutectic of the alpha and beta solutions.

The sequence of events in the freezing of an alloy on the N-side of the series, such as $(q$-$q')$, should be evident from what has gone before, and no description of such will be attempted.

The components of the several fields are as follows:

   I. Melt.
  II. Melt and alpha solution.
 III. Melt and beta solution.
 IV. Solid alpha solution.
  V. Solid beta solution.
VIa. Solid alpha solution and eutectic (alpha and beta solutions).
VIb. Solid beta solution and eutectic (alpha and beta solutions).

Case c. *The Formation of Intermetallic Compounds.*—We have here two possibilities, in one, the compounds are wholly insoluble in one or both of the pure metals, and in the other, they are partially soluble. We thus have two variations of cases a and b, respectively; as a matter of fact, there is nothing new presented by the equilibrium diagram except the actual formation of the compound. We shall describe only the diagram of the limiting case of total solid insolubility (Fig. 21). This diagram is evi-

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[1] The outward flaring solid solubility lines, $(f''$-$f)$ and $(g''$-$g)$, indicate a lessened solid solubility with fall in temperature. For the present, we may neglect this feature of the diagram.

dently a double diagram of the Group IIa type. Metals M and N form a compound, M_xN_y, occurring at composition c', and melting at temperature t_c. The compound contains, thus, Mc' per cent of metal N and Nc' per cent of metal M. Like any other chemical compound, it is of invariant composition and it has a definite melting point. Its freezing-point curve is like that of any pure substance, like that of a pure metal, for example. For purposes of study of the equilibrium diagram in which a compound occurs, it is best to regard the compound as a distinct metallic entity—as, indeed, it is—endowed with the property of
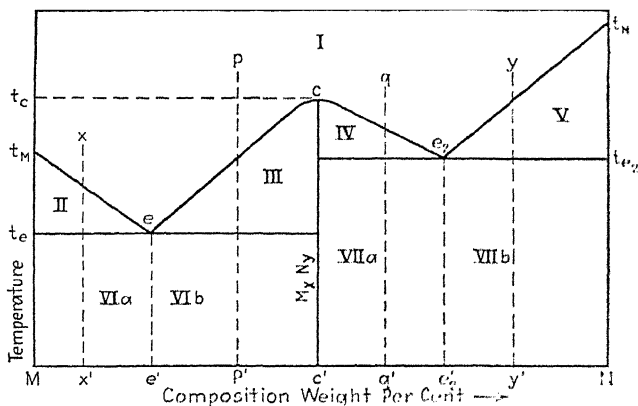
FIG. 21.—Equilibrium diagram of the metals M and N, which form a compound, M_xN_y. This compound forms a double eutectiferous series with the two metals, and are insoluble in them in the solid state.

constant melting point, of peculiar solubility powers, etc., such as would normally characterize an elemental metal. If we look at the matter in this light, the equilibrium diagram of Fig. 21 may be thought of as consisting of two abutting diagrams, contiguous at the line c-c', the composition of the compound. To the left of c-c', we have a simple diagram of Type IIa. Metal M and the compound M_xN_y—the two components of the system—are wholly insoluble in each other in the solid state. Metal and compound form an eutectic at Me' per cent of N, melting at temperature t_e. Alloys to the left of the eutectic composition consist, in the solid state, of metal M plus an eutectic of M and the compound; those to the right consist of the compound and the aforesaid eutectic.

The same general descriptions hold of the alloys to the right of (c-c'), only here the pure metal phase involved is N. N and the compound, M_xN_y, form an eutectic at Me_2' per cent of N which melts at temperature t_{e_2}. Solid alloys to the right of the eutectic (designated e_2, to differentiate it from e the eutectic of the compound and metal M) consist, obviously, of metal N and this eutectic e_2; those to the left, of M_xN_y and eutectic e_2.

An alloy exactly corresponding in composition to c', is, of course, 100 per cent compound (M_xN_y) after solidification.

The above description of the constituents of the various fields of the diagram, with the complete listing of them below, should make perfectly clear the precise sequence of events occurring when such typical compositions as (x-x'), (p-p'), etc., freeze or melt. No further discussion of this diagram seems, therefore, necessary. The several fields of the diagram are, however, made up as follows:

 I. Melt.
 II. Melt and solid M.
 III. Melt and solid M_xN_y.
 IV. Melt and solid M_xN_y.
 V. Melt and solid N.
 VIa. Solid M and eutectic e (M and M_xN_y).
 VIb. M_xN_y and eutectic e (M and M_xN_y).
 VIIa. M_xN_y and eutectic e_2 (N and M_xN_y).
 VIIb. Solid N and eutectic e_2 (N and M_xN_y).

The companion equilibrium diagram of the above, but of a series which shows some solid solubility between the compound and the metals, is that given in Fig. 22. The resemblance of this diagram to that of case b is striking and its interpretation should present no difficulty.

Group III. Alloys Whose Two Component Metals Exhibit Unlimited Intersolubility in the Liquid State, a Partial Solubility in the Solid State, and the Curves of Primary Solidification Intersect a Transition Point Which Corresponds to the Temperature of the Peritectic Reaction.—Like the alloys of Groups I and II, those here show complete liquid solubility; like the alloys of Group IIb, they show partial solid solubility. Differing, however, from any case of Group II, the curves of the liquidus of this series of alloys intersect, not at a minimum, but at a transition point, in temperature somewhere between the melting points of

the two metals. The temperature of intersection corresponds
to that of a reversible chemical reaction, called the *peritectic*
reaction. This reaction, on cooling, occurs between the solid
phase already formed (the properitectic phase) and the residual
melt, to form a new solid phase, either another solid solution, or
an intermetallic compound; from these two possibilities arise
the two subdivisions of the group.

*Case a.   The Product of the Peritectic Reaction Is a Solid Solu-
tion.*—The equilibrium diagram of this subclass of Group III is
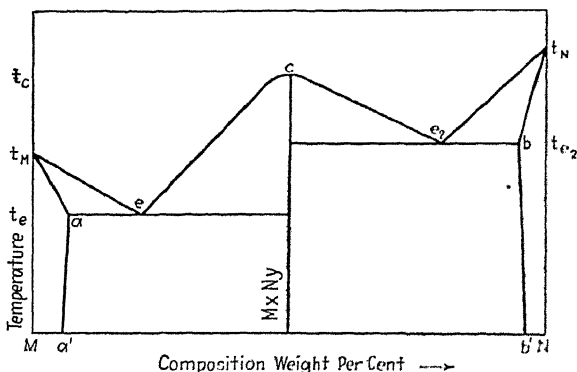
Fig. 22.—Equilibrium diagram of metals M and N, which form a compound
M_xN_y. This compound forms a double eutectiferous series with the two metals,
and is partially soluble in them in the solid state.

given in Fig. 23, and one can see that, in general features, it is
not very different from the diagram of Group I alloys. Indeed,
what little difference exists, centers around the point *o*, and
the line (*p-o-q*). The former is the peritectic point and the
latter is the peritectic horizontal. In the equilibrium diagram
of the Group I alloys, we have below the solidus a single series of
solid solutions. It is a continuous or isomorphous series, as it is
sometimes called. In the present diagram, we have below the
solidus a double or discontinuous series of solid solutions. The
diagram illustrates, also, in accordance with the definition of
the group, another instance of limited solid solubility, since solid
M can hold dissolved never more than Mp per cent of N; if that
amount is exceeded, a new phase, another solid solution, forms.

A description of the freezing of four typical compositions
follows:

a. (x-x'): The freezing of this composition follows the same course as any alloy of Group I. The solid alloy is the M-rich solid solution, designated the alpha solution.

b. (y-y'): Like the above, we are dealing with a simple case of solid-solution formation in the manner of Group I alloys. The solid solution forming is, necessarily, the N-rich solution, here called the beta solution.

c. (R-R'): Composition lying between points p and q, that is, those containing between Mp and Mq per cent of N, are the ones whose freezing behavior differs somewhat from anything yet described. We shall consider, first, any composition, as
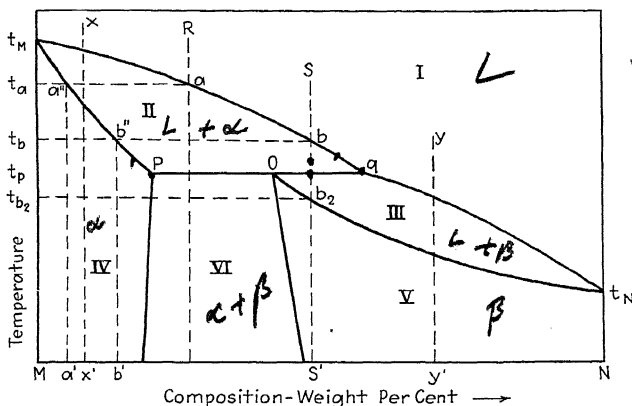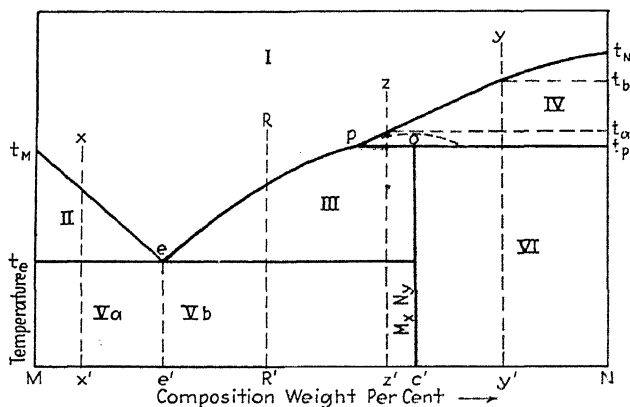

Fig. 23.—Equilibrium diagram of metals M and N, which are completely soluble in the liquid state, and partially so in the solid state. A peritectic reaction, on cooling, results in the formation of a solid solution.

(R-R'), lying between p and the peritectic point o. Freezing starts at temperature t_a as soon as the temperature drops to the liquidus. Crystals of the M-rich solution—the alpha solution—of composition Ma' per cent of N, form. Freezing continues as the temperature drops to the peritectic temperature t_p; the composition of the solid phase meanwhile varies along the solidus from a'' to p. During the same temperature interval, the melt, becoming proportionately enriched in N, moves in composition along the liquidus from a to q. At the peritectic temperature, t_p, a reaction occurs between the residual melt of q composition (Mq per cent of N) and the alpha solid solution of composition

p (Mp per cent of N), forming a new solid solution, the beta solution, of composition o (Mo per cent N). This reaction may be expressed as follows:

$$\text{Melt} + \text{alpha solution} \rightleftharpoons \text{beta solution}$$
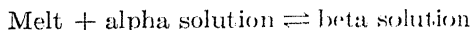
The reaction occurs at constant temperature, like that other three-phase (two-component) reaction at the eutectic point. On cooling, the reaction proceeds to the right till one of the reactants is completely utilized. In the compositions between points p and o, the reactant to become first exhausted is the melt. Consequently, the reaction carries on in the direction indicated till the alloy consists entirely of the newly formed beta solution plus whatever amount of the alpha solution is left; that is to say, on cooling, the reaction continues to the right till the alloy is completely frozen. Solidification is complete at t_p, and no further (assumed) change takes place on subsequent cooling to room temperatures.

d. (s-s'): This composition typical of all those within the peritectic range but to the right of the actual peritectic point, begins solidification at temperature t_b, with the deposition of crystals of the alpha solid solution. Crystals of such continue to separate out through the rather short temperature range to the peritectic temperature t_p. The composition of the melt, as always, varies in the meantime along the liquidus, from b to q, and that of the solid from b'' to p. These two phases of the compositions indicated react at temperature t_p, peritectically, to form as before a new (beta) solid solution of composition o. As in the previous instance, the reaction on cooling proceeds to the right till stopped by the exhaustion of one of the reactants, in this case, the alpha solution. Immediately below the peritectic horizontal, *i.e.*, just below t_p, the alloy consists of the newly formed beta solution and some residual melt. Unlike alloy (R-R'), the freezing of (s-s') is not completed when the peritectic reaction comes to a close; necessarily, this is so since one of two remaining phases at the end of the reaction is still liquid. Freezing continues—now no longer at constant temperature—to the solidus b_2, with the deposition of crystals of the beta solution. The completely solidified alloy consists of this solution only.

The several fields of the diagram are described as follows:

   I. Melt.
  II. Melt and alpha solid solution.
 III. Melt and beta solid solution.
 IV. Alpha solid solution.
  V. Beta solid solution.
 VI. Alpha and beta solid solutions.

Case b. The Product of the Peritectic Reaction Is an Inter-metallic Compound.—In the diagram of Group IIc alloys, the presence of an intermetallic compound in the series is indicated by a definite maximum on the liquidus curve at the composition of the compound. The presence of such a maximum point always denotes the formation of a compound. On the other hand, the absence of a maximum on the liquidus should not be interpreted to mean necessarily that compounds do not exist. Maxima, in this connection, are of positive diagnostic value only. A case in point is the present one. The equilibrium diagram of Group IIIb alloys (Fig. 24) exhibits no liquidus maximum, though an intermetallic compound of type formula M_xN_y actually occurs in the series. The reason for the absence here of the usual tell-tale maximum point on the liquidus is simple enough when the circumstances surrounding the origin of the compound are known. The compound actually forms subsequent to the *beginning* of freezing, and as it is only the initial events of solidification process that are recorded on the liquidus, the act of compound formation is not indicated there. And on heating, the compound dissociates before liquidus temperatures are reached, that is to say, its dissociation temperature is below its "melting point." Necessarily, evidence of a phase's dissolution, as that of its formation, are wanting on a curve which records higher temperature changes only.

The equilibrium diagram of this alloy series is shown in Fig. 24. The only compositions of the series, in the freezing of which novel behavior is displayed, are those within the peritectic range of composition, those lying between points p and pure N. Two such compositions are $(y\text{-}y')$ and $(z\text{-}z')$.

$(y\text{-}y')$: The compound occurs at $o\text{-}c'$ composition, alloy $(y\text{-}y')$ is, thus, to the right of both p and the compound vertical. Solidification begins at t_b with the separation of crystals of pure N; this continues as the temperature falls through the interval $t_b\text{-}t_p$. The melt, gradually impoverished

in N varies in composition along the liquidus to p. On cooling through temperature t_p, the peritectic reaction takes place; as in the previous case, this is a constant-temperature, reversible reaction, involving three phases. The new phase (on cooling) is the compound M_xN_y. The reaction may be represented as follows:

$$\text{Melt} + \text{solid } N \quad : M_xN_y$$
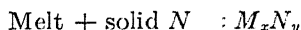
For all compositions richer in N than the composition of the compound, as $(y$-$y')$, the reaction, on cooling, proceeds to the

Fig. 24.—Equilibrium diagram of metals M and N, which are completely soluble in the liquid state and incompletely soluble in the solid state. A peritectic reaction, on cooling, results in the formation of a compound MN.

right till all the melt is consumed, the end of freezing is concurrent with the end of the peritectic reaction. The alloys are wholly solid just under t_p, and the solid alloys consist of a mixture of no especial arrangement or character of metal N and the compound, M_xN_y.

(z-z'): This composition, also to the right of the point p but to the left of the actual compound composition, begins to freeze at t_a, with the separation of solid N. Separation continues to t_p, the composition of the melt moving meanwhile along the liquidus to point p. At t_p occurs the peritectic reaction, wherein originates the compound. Solidification is still incomplete when the reaction comes to an end through exhaustion of properitectic solid N. The excess melt now freezes, with drop in

temperature to t_e, with further separation of compound. During this stage in freezing, the melt changes in composition along $p\text{-}e$. At temperature t_e, the eutectic forms in the usual manner; the eutectic consists of the compound and metal M.

The six fields of the diagram are structurally composed as follows:

    I. Melt.
    II. Melt and solid M.
    III. Melt and solid compound, M_xN_y.
    IV. Melt and solid N.
    Va. Metal M and eutectic (metal M and compound, M_xN_y).
    Vb. Compound, M_xN_y, and eutectic (metal M and compound, M_xN_y).
    VI. Metal N and compound, M_xN_y.

Group IV. Alloys Whose Two Component Metals Exhibit Limited (Partial) Intersolubility in Both the Liquid and Solid States.—All of the preceding alloy types had one common property, *viz.*, the component metals possessed unlimited liquid intersolubility at temperatures immediately preceding solidification. Alloys of Group IV differ, therefore, in this fundamental character, for they show a limited intersolubility at these temperatures. Because of an unlimited miscibility in the liquid condition, alloys of Groups I to III, inclusive, exhibit, irrespective of total composition, but one liquid phase—any molten alloy of any of these Groups is a single, homogeneous melt. Alloys of Group IV, on the other hand, show a single-layered melt only up to the limits of liquid solubility, when and if these limits are exceeded, a second layer (phase) puts in its appearance, immiscible with the first and separated from it by a definite interface. This hitherto nonexistent aspect of heterogeneous equilibria can again best be studied in connection with the equilibrium diagram of the series. This is given in Fig. 25.

At temperature t_p, liquid M can dissolve Mq per cent of molten N, and—on the other side of the diagram—molten N can dissolve Nq' per cent of M. At temperatures higher than t_p, as for instance, t_l, the solubility of each liquid metal in the other is somewhat increased, *viz.*, Ml' per cent of N, and Ns' per cent of M. In other words, there is the usual increase in liquid solubility with increase in temperature.

Liquid alloys whose total compositions are to the left of point p (Mq per cent of N, or less) consist, at the beginning of freezing, of a single-phase melt, and freezing follows in the usual manner and with the usual results. Likewise, the N-rich alloys, which contain Nq' per cent of M or less, are single-phase melts, and they solidify in the normal fashion. Alloy compositions falling in the range p-p' consist, when molten, of two
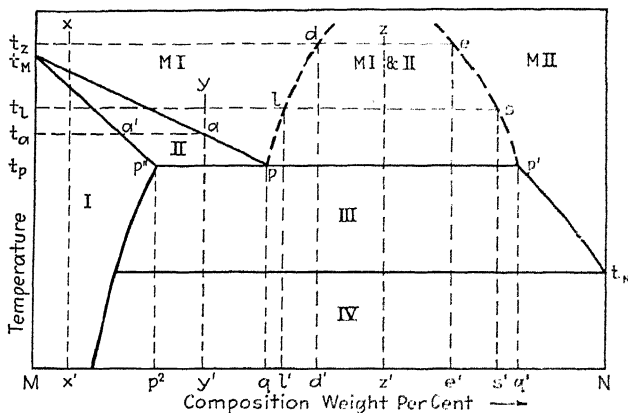
Fig. 25.—Equilibrium diagram of metals M and N, which are partially soluble in each other in both the liquid and solid states.

liquids, one, an M-rich solution containing, as a minimum concentration, Mq per cent of N, and the other, an N-rich solution, containing under similar conditions, Nq' per cent of M. Each solution is a quite separate and distinct entity as becomes any true physicochemical phase; when appreciable differences in specific gravity between the two solutions exist, the lighter of the two solutions of the undisturbed melt will float on the heavier one. These two immiscible liquids are called *conjugate solutions*.

The coexistence of the two conjugate solutions at temperatures above t_p affords an illustration of equilibrium between two dissimilar liquids,

While at t_p the compositions of the solutions are given by p and p', respectively, at higher temperatures these change in the

direction of increasing concentration of the solute metal. The composition varies along p-l for the MI solution, and along p'-s for the other, *i.e.*, they become with increasingly higher temperatures closer and closer in composition. It is conceivable that at some temperature (if actual boiling of either solution does not intervene) the compositions of the two solutions become identical; they would then lose their respective identities to merge into a single homogeneous solution. On cooling this single solution back through the critical temperature, reversion into a two-liquid melt would, of course, occur.

But one's interest, in a practical way, is not so much in the conditions prevailing in the liquid state as it is in those existing after solidification is complete; so to arrive at a knowledge as to what these latter conditions are and as to what manner of freezing produces them, we shall consider, as has been our custom, the solidification procedure of a few typical compositions, but now limiting ourselves to those compositions whose freezing manner is, in any way, peculiar.

$(y$-$y')$: This alloy, at temperature t_l, is a single-phase melt. Solidification begins at the liquidus t_a, with the separation of solid alpha solution of composition a'. Freezing continues to t_p, the composition of the solid solution moving meanwhile from a' to p'', that of the residual melt from a to p. Thus, at t_p, the alpha solution of composition p'' is in equilibrium with the melt MI of composition p. But if we follow the line p''-p-p' to the right, we find that these two are also in equilibrium with a third phase, MII of composition q'. We have, then, another three-phase system

$$\text{alpha solution} \leftrightharpoons M\text{I} \leftrightharpoons M\text{II}$$
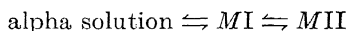
or expressed as a peritectic reaction,

$$M\text{I}_p \leftrightharpoons \text{alpha solution}_{p''} + M\text{II}_{p'}$$
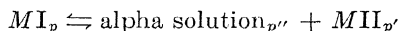
On cooling, the reaction proceeds to the right at constant temperature (hence the horizontality of p''-p-p') till one reactant (in this case, MI) is exhausted. Solidification, still incomplete at the cessation of the reaction because of the survival of MII, continues by further separation of the alpha solution but now, of course, from melt MII. The composition of the MII now varies along p'-t_N. When the latter's composition

actually reaches t_N, the melt has the composition of pure N, and the final act in the freezing process is the solidification of this at constant temperature. The solid alloy consists, then, of the alpha solution and metal N.

$(z\text{-}z')$: This composition consists, at the start, of two liquid phases MI and MII. At temperature t_z, the compositions of these two conjugate solutions in equilibrium with each other are represented by points d and e, respectively. With drop in temperature, the compositions of the solutions change along dp and ep'. At temperature t_p, the peritectic decomposition of MI occurs, giving rise to the first solid, crystals of the alpha solution.
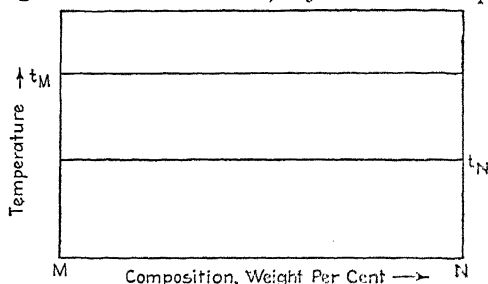
Fig. 26.—Equilibrium diagram of metals M and N, which exhibit no solubility for each other in either the liquid or solid state.

Freezing from this point on is similar to that followed by the $(y\text{-}y')$ composition.

The fields are described as follows:

   MI. Melt I.
   MII. Melt II.
MI and MII. Melt I and Melt II.
      I. Alpha solution.
      II. MI and alpha solution.
      III. MII and alpha solution.
      IV. Alpha solution and metal N.

Group V. Alloys Whose Two Component Metals Exhibit No Intersolubility in either the Liquid or Solid State. There is little that need be said concerning the freezing phenomena of this series of alloys, if alloys they are. The two metals exhibit slight if any liquid solubility for each other; there is, then, no effect of the one on the other's melting point nor, in fact, on any other circumstance of the freezing mechanism. Since intersolubility relations are never enhanced by freezing but if experi-

encing any change at all, it will always be in the opposite direction, the most that one can get in these "alloys" after solidification is a simple mixture, and unless special and often highly artificial conditions are not maintained during solidification, one does not get even this. The usual solidified product of two metals immiscible even when molten, is simply a layered solid of the two. One can hardly designate this an alloy, if the term "intimate association" of the definition has any significance at all. See Fig. 26 for the equilibrium diagram.

THE EQUILIBRIUM DIAGRAM: II. THE
SOLID ⇌ SOLID CHANGE

The precise manner and character of the liquid → solid change (freezing) is for most alloys of primary importance in giving form to the gross and fine structure of the alloy and in this way determining its general properties. But in certain alloys phase changes occurring subsequently to solidification may modify this initial structure and change in a greater or lesser degree the original properties. It may be unfortunate for the student of metallographic science that these changes in the solid state do occur, for at times they considerably complicate his problem of phase change-structure-property correlation, but practically they are of great importance. Because occurring last, they have the final opportunity of determining the eventual structure and properties of the alloy. Also, because of the comparative slowness and hesitancy of the changes themselves, they often become subject to influences from outside sources, for the existence of an appreciable time factor in many solid ⇌ solid changes provides the condition necessary to bring these changes within limits, of course—under man's purposeful control. For the present, we are interested in what these changes are, in what manner they manifest themselves, and how they can be fitted into the general picture of heterogeneous equilibria as given by the equilibrium diagram; we shall leave, for another occasion, the discussion of the interesting matter of their regulation.

Allotropic, or—as we shall more often say polymorphic changes, either of one of the metals or of some intermetallic phase, are responsible for most, though not for all, of the structural changes that take place in the solid state. We shall not attempt to classify these changes in so rigid a fashion as we did in the case of the changes incident to freezing and melting, but rather to discuss, in a brief manner, the following fairly typical examples:

1. One Metal Is Polymorphic. Considerable mutual solid solubility exists both above and below the polymorphic trans-

formation, but the transformation temperature is (a) lowered, or (b) raised, by the presence of the second metal in solution (depending presumably on the relative solubility of this metal in the two modifications). The equilibrium diagram of the subcase where lowering of the transformation temperature results from solution is shown in Fig. 27. M, of melting point t_M, is the polymorphic metal with the $M\alpha \rightleftharpoons M\beta$ change occurring at temperature t_m for the pure metal. Metal N (m.p. $= t_N$) forms (as the diagram is drawn) a continuous series of solid solutions with the high-tem-
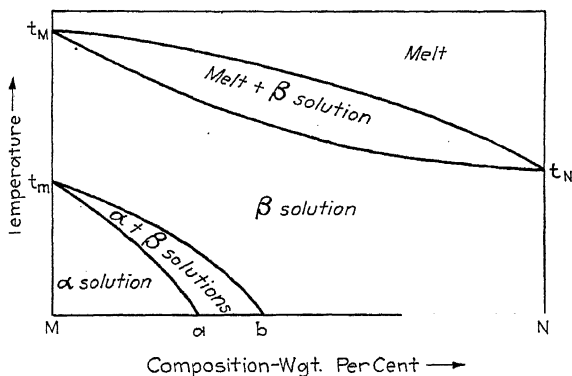
Fig. 27.—Equilibrium diagram of metals M and N, which form a continuous series of solid solutions. The transformation temperature of the polymorphic metal M is lowered by the presence of N in solid solution.

perature modification (beta) of metal M. The upper pair of curves is obviously the liquidus and the solidus of the diagram. Metal N lowers the transformation temperature of metal M, with increasing amounts of dissolved N up to Ma per cent; at the latter concentration, this temperature is depressed to room temperatures. Alloys whose compositions lie between pure M and Ma per cent of N possess at room temperatures the solvent M in the alpha modification, the usual, *i.e.*, the low-temperature, form in which this metal exists. Compositions richer in N than Ma per cent N contain at room temperatures some or all of metal M in its high temperature, or beta form. We have then at ordinary temperatures, for such alloy compositions, an example of a crystalline form existing at temperatures other than those where it is normally stable. The existence of $M\beta$ well outside its

customary temperature habitat constitutes a case of constitutional metastability.

Because of the comparative simplicity of the diagram, there seems to be no need for a detailed description of the cooling conduct of typical alloys of the series. The manner of the phase change on cooling (or heating) through the lower pair of curves (the major and the minor, so called) is not unlike that of the alloy cooling (or heating) between the liquidus and the solidus, except, of course, that the former change occurs wholly in the solid state.

The equilibrium diagram of the case where the transformation temperature is raised by the presence of the second metal is given in Fig. 28.
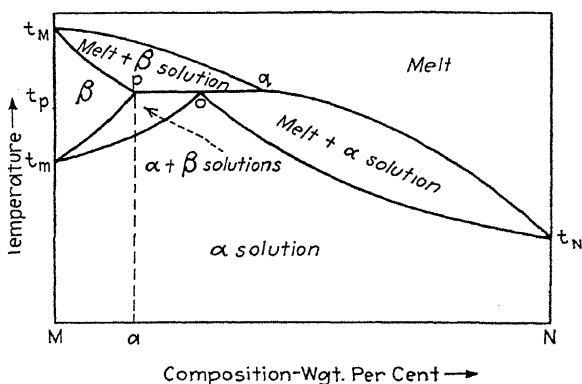
Fig. 28.—Equilibrium diagram of metals *M* and *N* which form a continuous series of solid solutions. The transformation temperature of the polymorphic metal *M* is raised by the presence of *N* in solid solution.

It seems more formidable in the matter of its interpretation than the preceding diagram. Actually, the peritectic reaction that is involved presents nothing novel. *M* is again the polymorphic metal with its transformation temperature at t_m. The presence of metal *N* in solution (assumably now because it is more soluble in *Mα* than in *Mβ*) raises this temperature to such an extent that with as little *Ma* per cent of *N* the major $(t_m\text{-}p)$ of the transformation curves intersects the solidus. The diagram reintroduces the peritectic reaction for point *o* is a peritectic point, the line *p-o-q* is a peritectic horizontal. Alloys of less concentration of *N* than *Ma* per cent freeze with the formation of the beta solution, that is to say, the solid solution in which *M*

is in the high-temperature form. On further cooling, this solid solution changes along t_m-p to the alpha solution. Compositions between p and o freeze likewise with the formation of the alpha solution, which, however, reacts with the residual melt at the peritectic temperature to form the beta solution. For this range of composition, the melt is exhausted in the reaction, and solidification is necessarily complete at the end of the reaction. On further cooling, the residual pro-peritectic beta solution changes to the alpha.
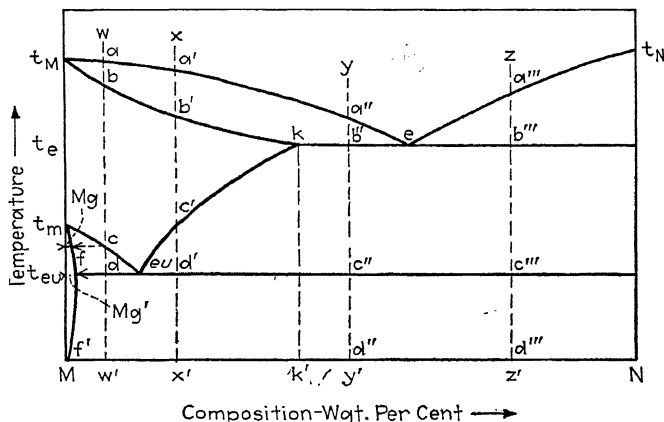
FIG. 29.—Equilibrium diagram of the metals M and N which show a considerable mutual solid solubility above the transformation temperature of the polymorphic M, but a very low solubility below that temperature.

All pro-peritectic beta of compositions to the right of point o disappear wholly during the peritectic reaction; these solutions are then not involved in a later polymorphic change.

A third case, differing somewhat from either of the above examples, is that one in which the considerable mutual solid solubility of the two metals prevailing above the transformation temperature is changed to one of low value below, indeed, the subtransformation-temperature value of solubility may become practically zero. Above the transformation temperature (see Fig. 29), the maximum solvent powers of M—the polymorphic metal—for metal N is Mk' per cent. This occurs at temperature t_e. At lower temperatures, the solid solubility decreases along line eu-k. Eventually, however, the progress of this solid solubility line toward decreasing solubility values is halted

by its intersection with another line, the phase-change line t_m-eu, coming in, with decreasing temperatures from the left. This last line is the temperature-composition curve of the polymorphic change of $M\alpha \leftrightarrows M\beta$. The meeting of these two lines at the point eu constitutes a minimum, an eutectic-like point quite appropriately called the *eutectoid* point. Similarly, the change on cooling occurring at eu is called the eutectoid inversion, the horizontal t_m-d'-c''-etc., is the eutectoid horizontal and t_{eu} is the eutectoid temperature. Compositions to the left of eu are designated hypo-eutectoid, those to the right hyper-eutectoid. The free or excess constituent in alloys, either to the right or left of the actual eutectoid composition, is called the pro-eutectoid phase.

The metallographic constitution of alloy w-w', for example, is pro-eutectoid $M\alpha$, and an eutectoid of $M\alpha$ and N. The latter has a composition (irrespective of the total composition of the alloy) of Meu per cent of N and Neu per cent of M. Like an eutectic, it is a diphasial mixture of definite proportions; it has also the lamellar appearance of many eutectics (see Fig. 79).

Because of the apparent complexity of the diagram and also because the iron-cementite system (steels and cast irons) belongs here, we might profitably follow through the events connected with the cooling of four typical compositions.

$(w$-$w')$: This is a typical hypo-eutectoid composition. Freezing occurs through the interval a-b, with the production of a solid solution of N in $M\beta$. At c, dissolution of this solution begins with the rejection of free (pro-eutectoid) $M\alpha$ (the $M\beta \rightarrow M\alpha$ change having been delayed till now because of the dissolved N), containing, however, a small amount—actually, Mg per cent—of dissolved N. This dissolution and separating process continues from c to d, with the composition of the residual solution moving from c to eu. At d (the eutectoid temperature) occurs the eutectoid inversion, where the residual solution of eutectoid composition changes into an aggregate of pure N, and $M\alpha$ containing a very small amount of dissolved N (Mg' per cent). The slight solvent powers of metal M surviving the polymorphic change become further reduced as the alloy cools to room temperatures. The alloy at room temperatures consists of pro-eutectoid $M\alpha$, in which Mf' per cent of N is dissolved, and the eutectoid of this extremely dilute solution and pure N.

x'): This hypereutectoid composition freezes over the interval a'-b'. The solid solution there formed begins to decompose at c', with the rejection of solid N (N, and not M, for we are to the right of the eutectoid point). This separation of N continues to d', while the enrichment of the solid solution in M proceeds along (c'-eu). At d' (temperature t_{eu}), the composition of the solid solution is such as to be saturated with both M and N, and concurrent separation of the two takes place. The alloy at room temperatures consists of free N, and the usual eutectoid of N and $M\alpha$ (with Mf' per cent of dissolved N).

$(y$-$y')$: This represents a hypo-eutectic composition. The freezing of the pro-eutectic solid solution occurs through the interval a''-b''. By the time point b'' is reached, the composition of the solid phase is given by the point k, and that of the residual melt in equilibrium with the solid by point e. Lowering the temperature below b'' (temperature t_e) results in the formation of the eutectic. This consists, at the end of solidification, of pure N and the solution (saturated) of $M\beta$ and N. As the temperature further drops to c'', all solid solution, pro-eutectic as well as eutectic, becomes less and less concentrated with N, *i.e.*, solid N is precipitated along k-eu. The solid solution of Mk' per cent of N at b'' becomes Meu' per cent of N concentration at c''. Cooling slightly below c'' causes this solid solution to invert to the eutectoid, consisting of an aggregate of N and $M\alpha$ (with Mg' per cent of dissolved N).

The varying manner of the formation of N and the different temperature levels at which it forms naturally affect somewhat its mode of distribution in the alloy; also, when the phase is not an element as is the case here, but a compound, the stability of the phase is often influenced by the temperature conditions prevailing at the time of its formation.

$(z$-$z')$: Pro-eutectic N freezes out of this hypereutectic alloy during a'''-b''', the composition of the melt moving meanwhile to e. Cooling below b''' forms the eutectic of metal N and the solid solution of M with Mk' per cent of N. Cooling the solid alloy further to c''' results in the separation of solid N along the line k-eu. At c''' the eutectoid forms, as in the three previous cases.

The alloy below t_e, is composed of solid N and the eutectoid. The N of the alloy (of all alloys to the right of point e) originates in the following ways:

1. The formation of the pro-eutectic phase from a''' to b'''.
2. The formation of the eutectic at t_c.
3. The separation of N from the solid solution from t_c to t_{cu}.
4. The formation of the eutectoid at t_{cu}.[1]

2. An Intermetallic Phase Is Polymorphic.—All of the above-described changes were the result of polymorphic changes in one of the metals of the series. In some alloys, polymorphism involves an intermetallic phase rather than the pure metals, and that is the condition with which we are here concerned. These polymorphic intermetallic phases are, for the most part, intermediate solid solutions, usually of peritectic
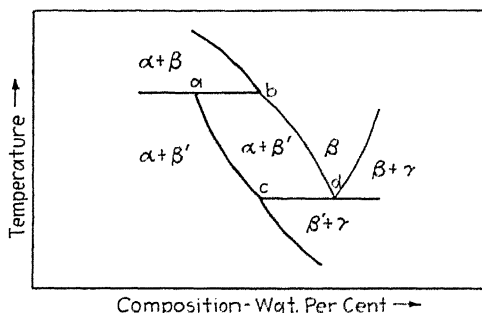
FIG. 30.- -Portion of an equilibrium diagram showing a polymorphic change in an intermetallic phase.   (After Hoyt.)

origin, and possessing a complex lattice structure of no especial stability. These solid solutions undergo, in many instances, structural changes at low temperatures that are in all essentials polymorphic in character. These intermediate solid solutions, unlike the terminal solutions of a series, have a lattice structure quite unlike that of either of the two component metals. It would seem, then, that the polymorphism of the intermediate solution is in no obvious way connected with elemental allotropy. At the present stage in the development of the science, the changes which some of these complex intermetallic phases may undergo are not at all clear.

[1] To these, a fifth source might be added.   The circumstance that the M phase below t_{cu} is not pure M but an extremely dilute solution of N and $M\alpha$, which becomes more dilute still with decreasing temperatures, implies precipitation of solid N, in minute quantities, below the eutectoid temperatures.

The graphic representation of one type of change described is shown in Fig. 30. Only that part of the whole diagram which deals with the change under discussion is given. The high-temperature form of the intermediate solid solution (β) passes into the low-temperature form (designated β') at inconstant temperature. The composition of β' varies along $a\text{-}c$, the coexisting β phase meanwhile varies along $b\text{-}d$.

TERNARY EQUILIBRIA

Alloys are by no means limited to two component metals; indeed, many of our most serviceable alloys contain, three, four, or even more metals and nonmetallic elements. The graphic representation of ternary and higher order equilibria, even where these are known and understood, is no simple matter. Yet no new principles are introduced, and so we shall confine our discussion to a single illustrative example. We shall, for this purpose, take the ternary system of L, M, and N, three hypothetical metals, which we shall assume possess complete solubility in the liquid state, but which are completely insoluble in each other in the solid state. This case is, thus, analogous to the binary Group IIa alloys.
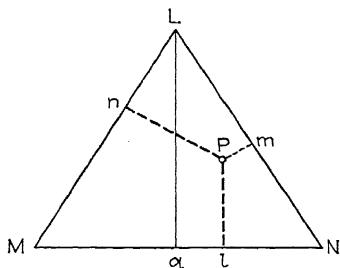
Fig. 31.—Graphic representation of composition in a ternary system (Method I). (*Adapted from Rhodes' "Phase Rule Studies."*)[1]

In a binary system, we required one direction (coordinate) to represent composition; here we need two. The amount of the third metal can be determined by subtracting the sum of the other two from 100 per cent. The composition plot is made along the three sides of an equilateral triangle. In this geometrical figure the sum of the perpendicular distances of any point within the triangle to the three sides of the triangle is equal to the height of the triangle; for example, in Fig. 31, $lp + np + mp = Lq$. If we make the height of the triangle equal to 100 units and have each corner represent 100 per cent of the pure metal, then the composition of the alloy p is np per cent of metal N, mp per cent of metal M, and lp per cent of metal L. Again, instead of measuring composition distances

[1] From ˉRhodes' "Phase Rule Studies," Oxford University Press, by permission of the publishers.

from the point p vertically to the three sides, we may make use of another property of the triangle to measure these distances by lines drawn through p parallel to the triangle sides, as is done in Fig. 32. The distances then measured from p to the sides,
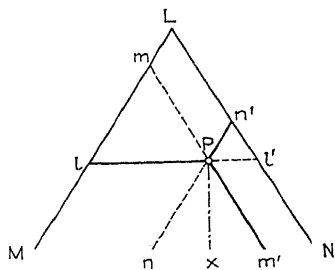
FIG. 32.—Graphic representation of composition in a ternary system (Method II). (*Adapted from Rhodes' "Phase Rule Studies."*)[1]

as for example, line pn for the L content of alloy p, are $2/\sqrt{3}$ times those measured in the former method (line $pn = 2/\sqrt{3}$ line px).

In this second scheme, composition in 100 units is marked off along each of the three sides of the triangle, with the pure metals, L, M, and N, at the corners, as before, but instead of measuring distances to the sides normally, we do so along three lines drawn parallel to the three sides. In this way, point (alloy) p, represents pn' per cent of M, pl per cent of N, and pm' per cent of L.

Either of the two schematic methods described concerns itself with the graphic representation of composition relations
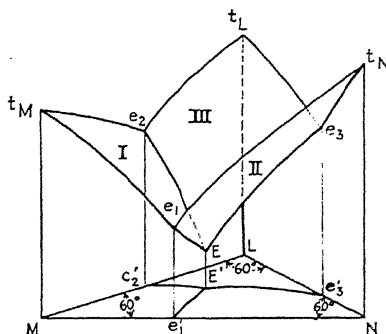
FIG. 33.—A polythermal (space) model of a ternary system. (*Adapted from Rhodes' "Phase Rule Studies."*)[1]

only. Each is an *isothermal* diagram representating equilibria at a single temperature. Obviously, to make the system's equilibrium picture a complete whole, all of the temperatures involved, *i.e.*, all temperatures between ordinary temperatures and those where fusion merges all components into one homogeneous melt,

[1] From Rhodes' "Phase Rule Studies," Oxford University Press, by permission of the publishers.

should be included. To do this requires the use of a third dimension; that is to say, a *polythermal* diagram of ternary equilibria is a solid model. Such a model of the ternary system, L, M, and N, under the solubility conditions as stated in the opening paragraph, is shown in Fig. 33.

The model is a triangular prism, with compositions plotted along the triangular base according to the second described method of reckoning. Temperatures are plotted vertically; thus t_L is the melting point of metal L, t_M of metal M, and t_N of metal N.

The V-shaped curve t_M-e_2-t_L, is the eutectic curve (liquidus) of the binary L-M series, its arm t_M-e_2 marks the beginning of the separation of solid M from the alloys containing only L and M. Likewise t_M-e_1 of the liquidus t_M-e_1-t_N marks the beginning of the separation of solid M from the binary M-N alloys. Surface I of the model is thus the solidification surface of metal M in the ternary melt. Surface II, by a similar line of reasoning, becomes the saturation surface of metal N, and surface III the saturation surface of L. The side,

$$t_M\text{-}M\text{-}N\text{-}t_N,$$

represents alloys of M and N only, with the binary eutectic at e_1. The liquidi t_M-e_1 and t_N-e_1, limits of the saturation surfaces I and II, intersect at e_1, while the equilibrium surfaces themselves meet along a line connecting e_1 with a lower point E—the ternary eutectic point. Surfaces I and II are saturation surfaces with respect to M and N, respectively; then on all points along e_1-E are solid solutions necessarily saturated with both metals. Similarly, one finds that e_2-E is the saturation line of metals L and M, and e_3-E that of metals L and N. The convergence of the three eutectic valleys at a single point, the triple intersection at point E, constitutes the ternary eutectic point. The alloy of the series whose composition occurs exactly at this point (E' of the triangular base) has the lowest melting point. Like its binary sisters, the ternary eutectic point represents a constant-temperature change.

In the solid model, horizontal sections may be taken at any temperature level. The sections so taken become isothermal diagrams. A number of such isothermal diagrams taken from the space model of Fig. 33 are given in Fig. 34. In a of the

latter figure is shown the isothermal diagram at a temperature *just above* the tereutectic temperature. The other sections from the same model, *b* to *e* inclusive, are taken at increasingly higher temperatures. The field outside the shaded area in each case represents compositions which are solid at the temperature in question.

To illustrate further the method of graphic presentation of data concerning equilibria in a ternary system, let us observe the the manner of freezing of a typical alloy. We shall take an alloy composition of a system such as we have been describing,
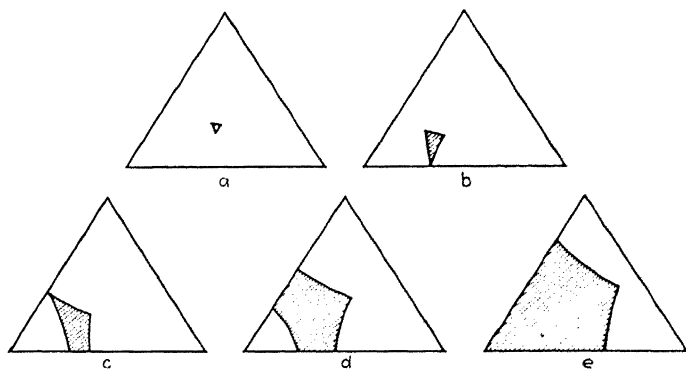
Fig. 34.—Horizontal (isothermal) sections through space model of Fig. 33. (*After Rhodes.*)[1]

i.e., a system whose components, the metals *L*, *M*, and *N*, are completely soluble in each other above freezing, while completely insoluble below. However, instead of using a three-dimensional model as the subject, we shall study the progress of solidification of the ternary alloy on a projection of the model. The projection, we shall find, is a much more satisfactory and convenient form of a working model than is the space model itself. At the same time, the change over from thinking in terms of a solid model to those of its projected form is not difficult. One common method of planary projection (Schreinmaker's) of the solid model is illustrated in Fig. 35. In this projection method, the compositions are plotted as usual along the sides of an equilateral triangle with the pure components at the three corners. Three heavy intersecting lines mark the positions of the eutectic valleys, the e_1-*E*, e_2-*E*, and e_3-*E* of the solid model. The

[1] From Rhodes' "Phase Rule Studies," Oxford University Press, by permission of the publishers.

dotted lines are isotherms, representing the contours of the three solidification surfaces of the model. The projection is, in fact, a "contour map." The comparative slopes of the three solidification surfaces are readily obvious.

On this projection we shall trace the progress of the cooling of a representative alloy, such as one of composition X (see Fig. 35). This alloy (Xl per cent of L, Xm per cent of M, and Xn per cent of N) is molten above temperature t. Solidification begins as soon as the temperature falls below t, with the separation of solid L from the ternary melt, for the composition X lies on the saturation surface (III) of that metal. As freezing

FIG. 35.—Schreinmaker's projection of space model of Fig. 36.   (*After Rhodes.*)[1]

continues below t, with further precipitation of solid L, the melt becomes gradually impoverished in that metal, its composition moving away from L along the line Lx'—a straight line drawn through L and point X. At point p this line intersects the valley contour e_3-E, which is the boundary of the L and N saturation surfaces, and metal N as well as L now freezes out. From p, the composition of the melt, now growing gradually less and less dilute with both L and N as temperature continues to drop, moves along e_3-E to the point E. At this point, the third saturation surface, I—that of metal M—is intercepted, and at this point all three metals freeze simultaneously; that is to say, a ternary eutectic forms at E. This is the final act of solidification. The wholly solid alloy consists of crystals of pure metal L, of an eutectic of L and N, and of a tereutectic of L, M, and N.

[1] From Rhodes' "Phase Rule Studies," Oxford University Press, by permission of the publishers.

The Phase Rule of Gibbs.—The concluding paragraphs of a two-chapter-long discussion of heterogeneous equilibria of type alloy systems could not be more profitably utilized than by devoting it to a brief exposition of two generalizations that have proved of signal service in the study of equilibria in all manner of heterogeneous systems. The first and more important of these is the phase rule of Gibbs, the other the LeChatelier-Braun principle. We shall consider the former first.

In this and the preceding chapter's discussion of phase reactions as exemplified in alloys, one, on occasion, may have wondered whether nature sets any limit to the number of phases that, under a given set of conditions, can coexist in equilibrium in any particular system, one may have asked oneself if there might not exist some limiting numerical relationship between the participating elements of a reacting system, on the one hand, and the determining factors of temperature, phase concentration, etc., on the other. One's curiosity in these matters would very likely have led one to the early observation that there never were more than three phases present at any one time in the binary systems under study, and that the presence of three was only occasional; indeed, it occurred only on the rarely prevailing condition when the temperature of the system remained constant while its energy content changed. Now, the phase rule gives us the answer to this and to many other puzzling aspects of equilibrium that our study of equilibrium diagrams may have brought to our attention, for it serves as a general guide as to the conditions under which equilibrium may exist in a polyphase system.

Before giving the phase rule, either as a formally worded statement or in the more convenient equation form, it might be well if we had clearly in mind what the various terms therein mentioned specifically mean. Some of these words and terms—perhaps, most of them—have been used from time to time in former discussions, where it seemed that the context would make their meaning obvious. Now, we shall chance no possible misinterpretation, and the following terms are defined according to physicochemical usage: *equilibrium, system, component, phase,* and the *variability* or the *degree of freedom* of a system.

Reactions involving change of state (also others) are reversible reactions. Under one set of conditions, the reaction proceeds in one direction, while under another set the reaction may be made

to proceed in the opposite direction. Conceivably, conditions may prevail so that the tendency to move in one direction may be exactly offset by the tendency to proceed in the opposite direction. The reaction is then, said to be *in equilibrium.* Equilibrium is thus a condition of no *net* change.

One particular group of reactants, operating under one set of conditions, constitutes a physiochemical *system.* An ice-water mixture existing at 0°C. and a pressure of 1 atm. is an example of a system. Further definition of the term is (Rhodes): "A definite space containing one or more substances, and these only, at one definite temperature and pressure, constitutes a system."

A *component* of a system is a chemical entity—an element or a compound. In the general cases discussed in this and in the preceding chapters, the components of the systems have been the hypothetical metals M and N (and L). In the ice-water system, previously mentioned, the compound H_2O is the component. Rhodes[1] has this to say concerning "components:"

The components of a system may be chosen sometimes in more than one way, but as it is the number of components that matters, not what they are, their choice is severely limited by two considerations. (1) The components must not decompose into simpler forms at any of the temperatures or pressures to be used, or in any of the reactions involved. (2) Their number must be the least possible consistent with condition (1). Thus in studying water, the components are not two, hydrogen and oxygen, but one, *viz.*, water, for water does not dissociate appreciably into oxygen and hydrogen until much above the temperature at which liquid water can exist at all.

Binary alloys are, thus, two-component systems, ternary alloys are three-component systems, and the water-ice mixture is an example of a one-component system.

A *phase* is any physically distinct, homogeneous, and mechanically separable portion of a system. At the temperature t_M, the melting point of metal M at a pressure of 1 atm., solid M and liquid M coexist indefinitely; solid M and liquid M each constitute a phase of the system for each answers *all* of the several requirements of the foregoing definition. Each is a physically distinct entity since it is separated from the other phase by definite physical boundaries; each is chemically homogeneous, and each may

[1] RHODES, "Phase Rule Studies," Oxford University Press, 1933.

be separated from the other by purely physical means, as by ladling out the solid or by draining off the liquid.

In alloys forming single melts, any composition above the liquidus constitutes a single phase; on cooling through the heterogeneous field, two phases are present, melt and solid.   Below the solidus, the circumstances of the solidification process necessarily determine the number of the phases present.   Alloys which freeze with the formation of a continuous series of solid solutions (Group I) have but one phase in the solid state.   Where solid solubility is limited (Groups II*b* and III*a*), the solid alloys may consist of two phases, both solid solutions.   In the case where no solid solubility at all exists, there may also be two phases, as for example, in alloys of Group II*b*.   In alloy systems where an intermetallic compound is present, the compound is a phase. Eutectic, eutectoid, and peritectic reactions involve three phases.

In a general physicochemical system, the external, independently variable factors which determine the equilibrium are three in number—pressure, temperature, and phase concentration (composition).   In alloy systems, however, we commonly neglect the vapor phase since, at the temperatures ordinarily involved, the amount of this phase and its pressure (in comparison to the total pressure exerted on the system) are small and inconsequential; accordingly, we usually assume that the pressure remains constant, hence ineffective in shaping equilibrium change. This leaves only temperature and phase concentration as actively involved in determining equilibrium in such (condensed, as they are called) systems.   There exists, in many cases, some latitude in the way these two variables may be shifted about without disturbing the equilibrium of the system, that is to say, without causing one or more of the phases of the system to disappear. The number of these variables that can be independently varied without disrupting the phase status quo of the system is known as the *variability* or *the degree of freedom* of the system.   In condensed systems, the variability obviously can never exceed 2. It may be 2, or 1, or 0.   Systems which show no degree of freedom are said to be invariant, those showing a single degree are called univariant, and those showing a maximum of two degrees are said to bivariant.

The phase rule gives the relationship between the number of phases that can exist in a system in terms of the number of the

components and the degrees of freedom or variability of the system. The rule is as follows: The number of the phases added to the degrees of freedom is equal to the number of the components plus 2. Stated algebraically, the rule becomes

$$P + F = C + 2$$

where P = the number of phases, F = the degrees of freedom, and C = the number of the components.

The above statement of the rule is for physicochemical systems, in general, for those wherein all three variables are operative. In condensed systems, the absence of the pressure factor automatically removes one degree of freedom, so $(C + 1)$ and not $(C + 2)$ becomes the quantity to the right of the equality sign. The equation, thus modified for alloy systems, is

$$P + F = C + 1$$

The best way to understand the rule is to apply it to actual cases; as one example where the application of the rule may be illuminating is the now familiar ice-water system. At 0°C., and under a pressure of 1 atm., ice and water coexist,

$$H_2O_{liq} \rightleftharpoons H_2O_{sol}$$
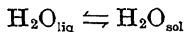
It is a one-component, two-phase system. The degree of freedom of the system can be determined as unity, from the following:[1]

The system is univariant; this simply means that at 0°C. water and ice can coexist only at one pressure, *viz.*, 1 atm. If the temperature is changed from 0°C., thereby exercising the single degree of freedom, the pressure becomes automatically fixed at another value, *i.e.*, it does if the two-phase equilibrium is to he retained. The same is true if one utilizes the one degree of freedom to change the pressure on the system. Then the temperature where the two phases can continue in contiguous existence becomes another definite value, quite outside man's control. That is to say that *either* the temperature or the pressure of this univariant system may be independently varied, but never the

[1] Strictly speaking this is a three-phase, hence invariant, system since the vapor phase is not entirely absent.

two at any one time; the choosing of what one shall be, automatically determines the value of the other.

All of the foregoing applies, of course, only if the system is to remain intact, that no phase is to disappear. To raise the temperature of the ice-water system above 0°C., while maintaining the pressure at 1 atm., will result in the melting of the ice; to lower the temperature, under the same circumstances, will result in the freezing of the water. In either case, one of the phases disappears. To preserve a biphasial equilibrium in the system, one variable and one alone, may be chosen for variation.

As further illustrative of the application of the phase rule, let
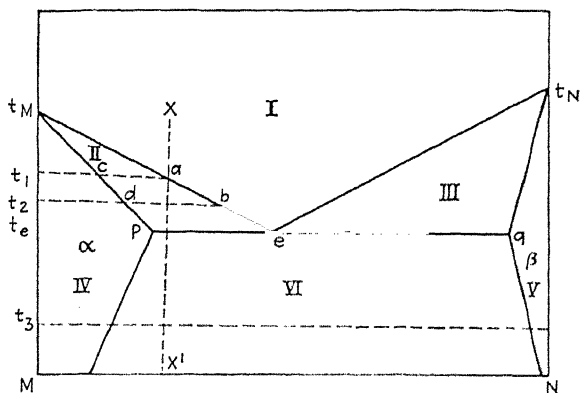
Fig. 36.— The phasial relationships in the alloys of Group II*b*.

us make use of Fig. 36, which is a reproduction of the equilibrium diagram of the Group II*b* series. The series (of metals *M* and *N*) shows complete liquid solubility and a partial solid solubility which grows more and more dilute with falling temperatures. The two terminal solid solutions (alpha and beta) form an eutectic at temperature *t*, and at composition *e*.

Since we are dealing with a condensed system, the modified equation of the phase rule is applicable: $F + C = P + 1$.

Field II is a two-phase field: the melt and the solid solution. The components of the system, metals *M* and *N*, are two in number. The variability of the system in this field is thus one, for $F + 2 = 2 + 1$, or $F = 1$. This means that we can vary, at will, either the temperature or the phase concentration, but not both. Let us see how this univariance works out in practice.

Alloy $(x\text{-}x')$ at temperature t_1 has just begun to freeze; the least bit of solid has formed. At this temperature, this bit of solid solution of composition c is in equilibrium with the melt of composition a, as

Alpha solution $\rightleftharpoons$ melt
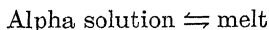
Now, if we use the single degree of freedom that nature has allotted to us to change the temperature, say, to a lower temperature t_2, the concentration (composition) of the two phases changes to d and to b, respectively. Thus, by fixing the temperature, one also fixes the concentrations of the two coexisting phases, or looking at it from the other side of the equilibrium picture, a solid phase of composition c can exist in equilibrium with a liquid of composition a only at temperature t_1. To change either the temperature or the phase concentration will result inevitably in an automatic and proportionate readjustment of the other variable.

Field VI is likewise a two-phase field for the two solid solutions, alpha and beta, are present. This is also a univariant field since at any temperature, as t_3, the concentration of each of the two solutions is exact and definite.

The point e is an invariant point, for we have there an equilibrium in which there are three participating phases. The reaction at e, if we remember, is as follows:

Alpha solution $+$ beta solution $\rightleftharpoons$ melt
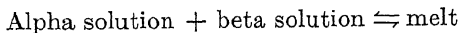
and the phase rule equation becomes $F + 3 = 2 + 1$, that is, $F = 0$. Thus, one has no choice in the matter; the composition of each of the reacting phases is fixed and definite, and the temperature is likewise fixed and definite. For one to change either the phase concentrations *or* the temperature will result inevitably in the destruction of one or more of the phases.

Fields I, IV, and V are single-phase fields and are therefore bivariant, for $F + 1 = 2 + 1$, or $F = 2$. Strictly speaking, however, the phase rule is not applicable to single-phase systems.

In the ternary system, L, M, and N (see model of Fig. 33), the ternary eutectic point E is an invariant point. There are four phases—three solid (metals L, M, and N), and the melt—and three components. Thus, $F + 4 = 3 + 1$, or $F = 0$. But, it should be noted that the eutectic valleys, $e_1\text{-}E$, $e_2\text{-}E$, and $e_3\text{-}E$ are univariant, although the limiting compositions, e_1, e_2,

and e_3, on the one hand, and E on the other, represent invariant systems. Compositions along any eutectic valley are univariant, for they are three-component three-phase systems. The saturation surfaces I, II, III are bivariant.

In conclusion, it must be emphasized that the phase rule is not applicable to systems not in equilibrium. The only possible value—indeed, the only legitimate use—of the rule in studying multiphase systems not in equilibrium is in the checking of the nonequilibrium character. If the number of phases present is more than the rule calls for, it becomes a certainty that the system is still unstable, or perhaps metastable.

LeChatelier-Braun Principle.—The phase rule, which concerns itself with the conditions under which the phases of a physicochemical system may be in equilibrium, tells us, however, nothing about the *direction* of the equilibrium shift that occurs whenever the conditions determining the equilibrium are changed. We know, for example, from observation that when the temperature of an ice-water mixture is lowered below 0°C., meanwhile holding the pressure constant at 1 atm., it is the liquid which disappears, or that when the temperature is raised above 0°C., under constant pressure, it is the ice which melts. Our common experience in such matters tells unhesitatingly the direction of the equilibrium change ensuing from change in temperature, one way or the other. But such an empirical method necessarily fails us if the system in question happens to be one that lies outside our immediate experience. The LeChatelier-Braun principle provides us with a reliable guide for predicting, in any and all cases, the direction in which equilibrium will move with variation in the causal conditions. The principle may be stated in this way: When the conditions determining the equilibrium of a system are changed so that there results a readjustment of equilibrium, the equilibrium shifts in that direction which will most effectively resist the imposed change.

An example or two should make the principle clear. In the ice-water system, the observed effect of lowering the temperature below 0°C., the pressure meanwhile remaining constant, is the disappearance (freezing) of the liquid phase. The lowering of the temperature that is responsible for the freezing is, in turn, the result of a removal of some heat energy from the system, the freezing of the water is, on the other hand, an exothermic reaction;

heat energy is made available for the system's use. Thus the shift in the equilibrium is in that direction which will tend to nullify the newly imposed conditions.

The univariant system water $\leftrightarrows$ vapor (steam) is in equilibrium at 100°C., and at 1 atm. pressure. If the pressure of the system is raised, and the temperature remains unchanged at 100°C., the permissible degrees of freedom have been exceeded by one. Consequently the number of phases will be decreased by that
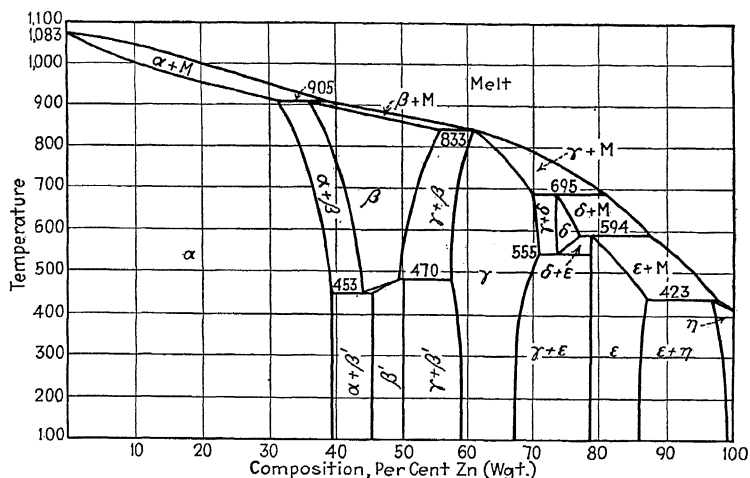
FIG. 37.—Equilibrium diagram of the copper-zinc system. (*After Bauer and Hansen*, 1927.)

number. The particular phase to disappear will be the vapor phase, for condensation works against the applied pressure, eases up the total pressure on the system, since a definite mass of the compound H_2O occupies less volume in the liquid than in the vapor state.

The Copper-Zinc and the Iron–Iron-Carbide Series.—Before leaving the matter of heterogeneous equilibrium, it might be well to devote some attention to the equilibrium diagrams of one or two actual alloy systems. Perhaps the two most important industrial alloy systems are (1) the copper-zinc series, which forms the basis of the brasses, and (2) the iron–iron-carbide series, the basis of the steels and the cast irons. The equilibrium diagrams of these two series are reproduced in Figs. 37 and 38.

At first glance, each appears unusually complicated and involved, but careful study will reveal that each is simply a composite of several features of one or more of the type diagrams that we have studied. Really nothing new is introduced in either diagram. A brief description of each diagram is given to assist in the interpretation.

Description of the Copper-Zinc Diagram.—There are five distinct solid solutions stable at room temperatures, a sixth (δ) is stable at temperatures above 555°C. There are five peritectic reactions in the series, one eutectoid inver-
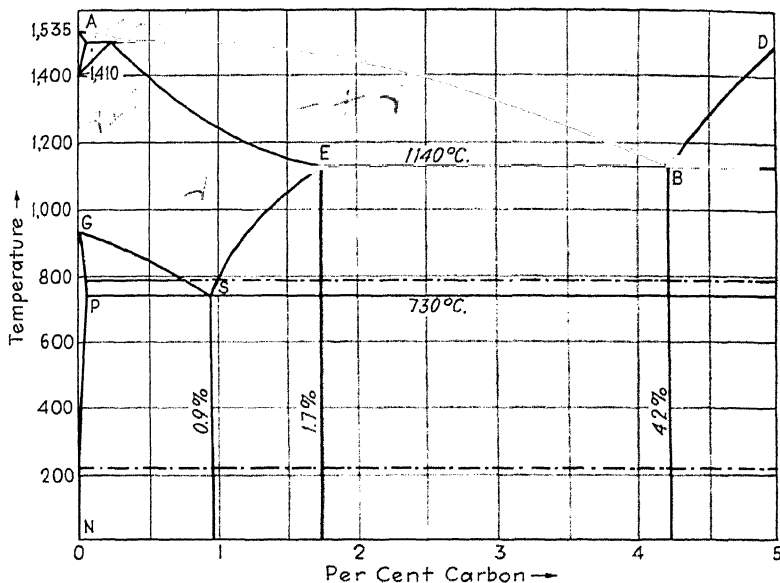
Fig. 38.—Equilibrium diagram of the iron–iron-carbide system.

sion, and one instance of the formation of a "superstructure."[1]   The origin of the six solid solutions is as follows:

The *alpha solution:* 0 to 39 per cent zinc; face-centered cubic lattice, ($a = 3.610$–3.688 Å.). Formed by primary crystallization (freezing) of the melt between 0 and 39 per cent zinc.

The *beta solution:* 39 to 59 per cent zinc; body-centered cubic lattice ($a = 2.95$ Å.). Formed (1) by the peritectic reaction at 905°C. (32.5–37 per cent zinc); and (2) by the primary crystallization of the melt (from 37 to 62 per cent zinc).

[1] See p. 125.

The *gamma solution:* 59 to 67 per cent zinc, complex cubic lattice of 52 atoms (a = 8.86 Å.). Originates as the result of (1) the peritectic re at 833°C. (56.5–62 per cent zinc); (2) the decomposition of the beta solu tion between 50 and 56.5 per cent zinc; (3) the primary crystallization of the melt from 62 to 81 per cent of zinc; and (4) the decomposition of the delta solution (the eutectoid inversion) between 72 and 75 per cent zinc.

The *delta solution:* 70 to 76 per cent zinc (above 555°C.). Originates as the result of (1) the peritectic reaction at 695°C. (70–81 per cent zinc); and (2) the primary crystallization of the melt from 81 to 88 per cent zinc.

The *epsilon solution:* 78 to 87 per cent zinc; hexagonal close-packed lattice (a = 2.75 Å.; c = 4.25 Å.). Originates as the result of (1) the eutectoid inversion at 555°C. and 73 per cent zinc; (2) the primary solidification of the melt between 78 and 98 per cent zinc; (3) the peritectic reaction at 594°C. (77 to 88 per cent zinc).

The *eta solution:* 87 to 100 per cent zinc; hexagonal close-packed lattice (a = 2.66 Å.; c = 4.93 Å.). Originates as the result of (1) the peritectic reaction at 425°C. (87 to 98 per cent zinc); and (2) the primary solidification of the melt between 97 and 100 per cent zinc.

Description of the Iron–Iron–Cementite Diagram.—The iron–iron-carbide series illustrates the occurrence of a peritectic reaction, the formation of an eutectic and an eutectoid, and the changes (in carbon solubility mainly) that result from two polymorphic transformations. There are also two magnetic changes shown, one in iron at a temperature somewhat under 800°C., and another in the iron carbide (Fe_3C) at about 215°C. It is interesting to note that the effect of increasing carbon is to raise sharply the temperature of the upper transformation ($\delta \rightleftharpoons \gamma$), to lower that of the change occurring a little above 900°C. in pure iron, and to have no appreciable effect on the position of the magnetic changes.

The ultimate phases present at room temperatures in any alloy of the series are *iron (ferrite)* (with a really very small amount of dissolved carbon), and *iron carbide (cementite)*.[1] But these two phases may occur differently in the several alloys. Only in the hypo-eutectoid alloys, that is, in those alloys with less than 0.90 per cent carbon, does ferrite exist as a distinct and separate metallographic constituent. This and the eutectoid (*pearlite*) are the two constituents present. In all other compositions of the series, ferrite is present simply as one component of the eutectoid. The iron carbide, or cementite, occurs as a free constituent in all compositions whose carbon content exceeds 0.90 per cent; of course, with ferrite, it is present in the pearlite in all of the alloys. The origin of the cementite of the different alloys varies. In the hypo-eutectoid alloys, where all the carbide is present in the pearlite, the cementite forms at the eutectoid inversion at temperatures above 700°C. In alloys whose compositions lie between 0.90 and 1.7 per cent carbon, the cementite exists partly as free cementite and partly as eutectoid cementite. The free cementite forms as the consequence of the precipitation of this phase from the iron (gamma)-carbon solid solution along the line *SE*. The eutectoid cementite forms, as before, by the change

[1] This statement, and subsequent ones, should be verified by reference to Fig. 38.

of the residual solid solution into pearlite at about 700°C. Alloys between 1.7 and 4.2 per cent carbon, *i.e.*, between the limit of maximum solubility of carbon in iron (gamma) and the eutectic point, have three varieties (as to origin) of the carbide, *viz.*, the eutectic cementite, the pro-eutectoid cementite (that forming along line *SE*), and the eutectoid cementite. The hyper-eutectic alloys, those richer in carbon than 4.2 per cent, possess cementite from these three sources, and that from an additional source, *viz.*, that forming on primary solidification along *BD*.

CHAPTER V

THE MICROCONSTITUENTS OF ALLOYS

The manner in which an alloy freezes chiefly determines its metallographic character and properties—this, and those changes that may occur in the solid alloy as it cools to room temperatures. In a few notable instances, as for example, when an eutectoid inversion is involved, these later occurring changes of the solid state are so devastating as quite to obliterate the original structure of the alloy, but, generally speaking, this is not so, and the much more usual consequence of a phase change in the solid alloy is a modification—perhaps, of some moment—rather than a complete dissolution of existing structures. Thus, for most alloys, one must go back to the particular events of solidification to find the source of its basic physical constitution. In spite of marked differences in freezing habit exhibited by the several type systems of alloys, and notwithstanding wide variations, in degree and in kind, of possible structural alterations that may follow freezing, there are surprisingly few primary microconstituents of solid alloys; in fact, there are but three, and of these, two have representatives that so closely resemble one another in some of their properties that one cannot always be sure that he is dealing with a bona fide member of one group or with that of the other. These three, more or less metallographically distinct, yet not always fundamentally distinguishable primary constituents of alloys are *pure metals, solid solutions,* and *intermetallic compounds.* An examination of the equilibrium diagrams of the typical alloy systems described in the two preceding chapters, relative to the actual phases present at room temperatures, will confirm this as the correct number and classification.

Our brief review (in Chaps. I and II) of what is known, or surmised, of the true nature of the metallic state was purposely confined to a description of the character and attributes of the pure metals. From that short discussion, one learned (*a*) of the essentially crystalline character of the metals, (*b*) of the existence

of a definite arrangement and spacing of the atoms of a metal, and (c) of the assumed presence of "free" electrons within the metal lattice. The last was really a unique feature of the metals. There mention only was made of another unique characteristic, *viz.*, a distinctive type of atomic bonding, the so-called "normal metallic kind of linkage." In this present chapter, where we shall have occasion to enlarge upon our notion of "metallicity" so as to include within the meaning of that term solid solutions and intermetallic compounds as well as the simple metals, we shall speak more explicitly, and at somewhat greater length, of this second, supposedly unique characteristic of metallic materials.

From the point of view of microstructure, some alloys are simply constituted, their gross structure is elementary, for they contain a single primary constituent. This may be a solid solution or, more rarely, an intermetallic compound. Other alloys possess a duplex structure, where two of the primary constituents (as two metals, two solid solutions, a metal and a compound, etc.) are present, and microscopically distinguishable. Still other alloys are more complex. The properties of a simply constituted alloy are necessarily those of the single constituent, modified, of course, by the alloy's granular characteristics, such as grain size, grain orientation, etc. The properties of a multiphase alloy are, however, not so easily described; it may possess properties that may approximate the average of the properties of the individual constituents, and again it may show considerable departure from the calculated mean, for frequently the manner of the association, *i.e.*, the particle size and number—the dispersion characteristics—of a constituent may be as important in determining the properties of the alloy as are the intrinsic properties of the constituent themselves.

We shall, in turn, consider each of the three primary microconstituents from two somewhat different points of view: First, we shall discuss the fundamental nature of each (this, in fact, has already been done in the case of the first constituent named—the pure metals), and secondly, we shall devote considerable attention to the matter of microstructure, that is, to the varied manifestations of the different constituents of metals and alloys as viewed under the metallographical microscope. In carrying out the first part of this twofold purpose, we shall make use of

anything that will aid us in definition or in identification; we shall find it again desirable to refer to metallic properties, in particular, as these relate to alloys.

THE PURE METALS

The nature and the fine structure of the pure metals have been discussed in Chaps. I and II, and seemingly adequately so;

Fig. 39a.—Very pure hydrogen-annealed iron. (*Photograph by Eppelsheimer.*)

Fig. 39b.—Electrolytic iron. Annealed. 100×. (*Photograph by*
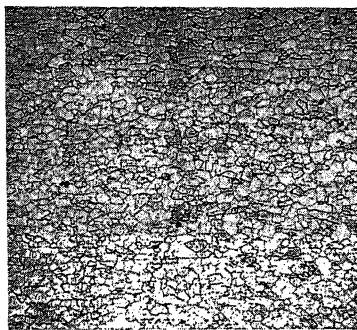
Fig. 40a.—Commercially pure iron. 100×.

Fig. 40b.—Commercially pure iron. 100×.

our present interest, therefore, will be mainly in a metal's microstructure.

Two photomicrographs of very pure iron are given in Figs. 39a and b; three photomicrographs of a commercially pure iron in Figs. 40a to 41a; and two photomicrographs of a still less pure iron

(really a mild steel with 0.08 per cent carbon) in Figs. 41*b* and 42. Perhaps, the difference most in evidence in these seven photomicrographs is in the size of the grains composing the aggregate. In Fig. 39*a*, the grains shown are uniformly large, so large, in fact, that, even at the low magnifications employed, only a portion of
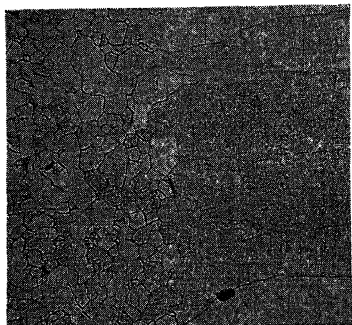
Fig. 41*a*.—Commercially pure iron. 100×.
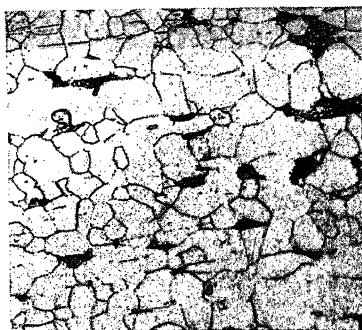
Fig. 41*b*.—Low-carbon steel.   100 ×.

three grains is included in the area photographed.   The grain size of the annealed electrolytic iron is also large (Fig. 39*b*).   The microstructures of the commercially pure iron (Figs. 40*a* to 41*a*)
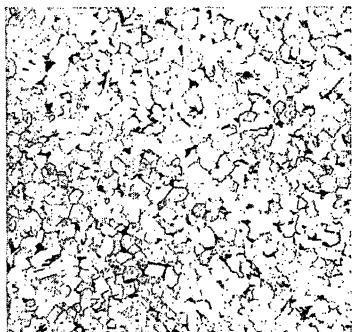
Fig. 42.—Low-carbon steel.   100×.

show that the samples photographed also varied considerably in grain size.   These grain-size differences in the several samples of the same material are the result of differences in previous treatment history.   The unusually large grains of the pure iron sample (of Fig. 39*a*) are also due to a thermal experience through which this particular metal has passed, and similarly—though because of an experience of another sort—is to be found the origin of the grain-size differences in one and the same sample— shown in Fig. 41*a*.   In the photomicrographs, the several crystalline grains are separated by hairlike boundary lines; the grains thus outlined are, in reality, allotriomorphic crystals of iron, or

ferrite (as iron is metallographically known),[1] and because these are three-dimensional affairs, the boundaries are enclosing films, or envelopes.   In Fig. 41*b*, we have a typical microstructure of a low-carbon iron-carbon alloy, a mild steel, containing about 0.08 per cent of carbon.   The light-colored areas are, of course, ferrite, and the darker ones are the carbon-containing areas (called *pearlite*).

Grain size (and *shape*) and *grain boundaries* are two obviously significant features of granular aggregates.   A third is *grain orientation*.   We shall begin our study of the microstructural characteristics of metal aggregates by describing each of these terms.   We shall consider orientation first.

Orientation.—In the photomicrograph of Fig. 39*a*, and also in that of Fig. 40*b*, one observes that there is some difference in the shading of the ferrite grains, that some are manifestly darker than others.   Apparently, the light corrosive attack (etching) was not exactly uniform over the entire surface of the specimen.   This condition cannot be due to any actual chemical nonuniformities in either the sample or in the etchant, but rather it is the result of a cooperative effect of what is, in kind, two heterogeneous conditions, of a purely *physical* nature, existing in the metal, *viz.*, (1) the anisotropism of the individual grains comprising the aggregate, and (2) a difference in the relative placement, or orientation of these grains within the aggregate.   The granular anisotropism—the first of the two mentioned—explains, as we have already learned, the directionalism in properties found in an individual crystalline grain; as an example of such might be cited the fact of the difference in electrical conductivity of a single copper crystal when this is measured in a direction parallel to a cube face (the 100 direction), and when it is measured at an angle to the face.   If all of the anisotropic grains of an aggregate were orientated alike, *i.e.*, if a particular plane of each crystallite (the 100 planes, for instance) showed a general parallelism throughout the mass of crystallites, any property directionalism exhibited by the individual crystallites would, necessarily, be passed along to the mass, and the aggregate, as a whole, would be

[1] Most of the microconstituents of the iron-carbon (or -cementite) series of alloys have been given specific names, the root of which if not descriptive, is derived from the name of some illustrious student of metallography; the ending is the usual mineralogical suffix *-ite*.

anisotropic, too. But such structural parallelism throughout crystalline masses is not of general occurrence, the far more usual thing is to find that the several grains of a polycrystalline metal are all differently positioned, or orientated with respect to any common crystallographic plane of reference. Thus, a random orientation of the crystallites of a metal produces the second type of structural heterogeneity mentioned above.

While the properties of a crystalline complex composed of anisotropic units orientated at random are definitely nondirectional, or isotropic, since *on the whole*, differences of the individual units cancel one another, it does not mean that these differences do not *locally* persist. They do; for example, if the polished surface of a plane section cut through a metal is brought in contact with a mild solvent (etchant), as has been done with the iron specimens, solution will occur faster—or at least, it will occur differently—on the exposed surfaces of some grains than on those of others.[1] Because of the difference in granular orientation, areas of somewhat varying susceptibility to chemical attack become exposed on sectioning, and there are, as a consequence, local differences in the rate, or in the manner, of attack, when the surface is etched. The exposed surfaces of some grains are so orientated that they become etched—in degree or in kind—so that when microscopically examined, it is found that most of the incident beam is dispersed, and that little light is returned through the tube of the microscope; these particular surfaces, as a result, appear darkened. Other surfaces, because of a different placement of the grains, respond to the etching attack, in a manner or to such an extent, that little dispersion occurs, with most of the light being reflected back into the microscope's field; these areas of the surface appear relatively light. And, of course, we can have many intermediate degrees of attack, and thus many different shadings between the extreme dark and light. A varying orientation of the grains, in effect, makes the action of the etchant a selective one.

While a random orientation of the constituent grains of a metal is the usual condition and may, therefore, be considered as the "normal" one, it is by no means true that this state always prevails. One finds, on occasion, granular aggregates whose

[1] For the mineral selenite ($CaSO_4 + 2H_2O$), the velocities of dissolution for the three faces 100, 110, and 111 are in the following ratio: 1 : 1.76 : 1.88.

crystallites depart considerably from a true helter-skelter arrangement, *i.e.*, where the grains, for one reason or another, assume a *preferred* orientation.   This does not mean that strict parallelism between the several grains exists—for this circumstance would imply the loss of granular identity—but rather that the grains tend toward this state of like orientation.   It is a condition that is usually imposed from without.

Grain Size and Shape.—Grain size is another term of metallographic significance, and also one of considerable technical importance.   The meaning of the term is obvious.   A grain is, of course, a three-dimensional affair, and a plane section through the grain, as through any of those photographed, shows but two of these; indirectly, however, if the number of grains present is sufficient to permit a statistical distribution, the section tells us something about the "missing" dimension.   A properly chosen section through a crystalline mass should then give one a fair notion of the average grain size of the sample.   This, in fact, is the way that grain size is commonly determined, and size is reported in area units, as for example, square millimeters. Plainly, such a measuring method cannot safely be applied to areas which have a small number of unequally sized grains.   A reliable evaluation of size in such specimens requires the exploration of large areas.

What are the causes—one asks—of the difference in grain size so manifest in the photomicrographs?   Quite naturally, grain size is the result of grain growth; but just why does grain growth proceed so differently in the different cases shown? · To answer fully such questions would be to discuss grain size origins with that detail and thoroughness that the importance of the subject justifies, and this would now lead us too far afield; nevertheless, a brief general statement concerning growth causes might be worth while.

At the outset, it is well to recognize clearly that some difference may exist between the mechanism and laws of crystal growth as these pertain to the birth and growth of crystals in melts during freezing, and those which control recrystallization in the solid state, as for example, the recrystallization of strain-hardened metal.   In both cases, however, the primal urge is the same, *viz.*, the tendency of all matter to assume the most stable form, *i.e.*, the one possessing the least internal energy.   This is, indeed, the

precise reason that crystallization occurs in the first place, for the crystalline state, as we have seen, represents a condition of lower energy content than the liquid state. In the former state of matter, the particular geometrical form of least internal energy is the one having least surface area per unit mass, that is to say, that the limiting condition of crystalline matter, as regards its energy state, is a single crystal of spherical shape.

With respect to the ultimate grain size of a cast metal (or alloy), there are, according to Tammann, two determining factors at

Nucleation Rate and Growth Rate
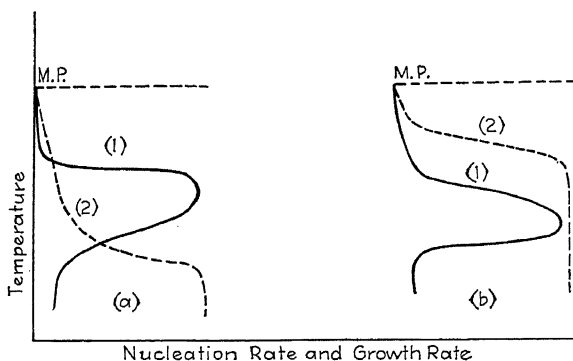
Fig. 43.—Two possible relationships between the nucleation rate (1), and the crystal growth rate (2). (*After Tammann.*)

work during the solidification process: one of these is the rate of nuclear formation, and the other is the rate of crystal growth. Whenever the latter, for any reason, becomes the more predominant factor in the process, there are relatively few centers of crystallization, but these few nuclei grow rapidly into a few large grains, and the resulting solid will possess a generally coarse-grained structure. On the other hand, if the rate of nucleation is rapid as compared with the growth rate, a large number of growing crystallites marks the progress of freezing almost from the start, and the final solid will be fine-grained. The rate at which nucleation proceeds in a melt—the nuclei number, as Tammann calls it—is small immediately below the freezing point, but increases with the degree of undercooling to a maximum (curves 1 of *a* and *b* in Fig. 43). The value of the nuclei number for the metals is very large, while for slags and glasses it is low: with the former, it is impossible, by varying the condi-

tions of solidification (as for example, its speed), to secure anything but a crystallized aggregate, while with the latter class of nonmetallic materials, the production of an undercooled liquid is more frequent than otherwise.

The second step concerned in crystallization is the growth of the several nuclei. The nuclear growth rate also increases as the temperature falls below the freezing point, attaining eventually a maximum which may be, as regards temperature, either below or above the maximum on the nuclei number curve (see curve 2 of *a* and *b* of Fig. 43). When the maximum growth rate is, in point of temperature, below the maximum rate of nucleation, as in (*a*) of Fig. 43, a large number of nuclei form, but any marked growth is delayed till somewhat lower temperatures are attained. A slow rate of cooling of the melt, therefore, brings a large number of nuclear crystals into the maximum growth range, and a fast rate only a small number. The first procedure obviously results in the production of the finer grained aggregate. When the maximum growth rate occurs earlier than the maximum rate at which the nuclei will grow [(*b*) of Fig. 43], nuclei start growing vigorously as fast as they form. A rapid rate of cooling of the melt is, then, conducive to a smaller average grain size, since the sooner the maximum-nucleation-rate range is reached, the more prominent nuclear formation becomes in comparison with nuclear growth.

The above statement that the final grain size of cast metals depends chiefly on the relative predominance of the rates of nucleation and crystal growth does not apply, without reservation, to cases where polymorphic changes occur in the metal or alloy, since these later changes are of some consequence in determining the final grain size of the material. The process whereby a new crystalline form, or even a new set of crystals of like form, is created from preexisting crystalline matter is known as *recrystallization*, a name which not only precisely describes the phenomenon but definitely allies it with its prototype, the formation of primary crystals from a melt. One common cause of recrystallization in metals and alloys is the occurrence of a polymorphic change. When a solid, polymorphic metal, of definite crystalline characteristics, including an average size of grain, cools to the transformation temperature, the original crystalline form becomes replaced by another that is quite new

and which possesses, in its own right, specific granular size and shape properties, though it may be true that some of the dimensional character of the old order is inherited by the new set of crystals.   This greater or lesser independence of the new crystalline aggregate from the parent one, in the matter of size of units, is found in the circumstance that recrystallization, like primary crystallization, is apparently nuclear in inception, that is to say, a crystal of one modification does not change into one of the other *en masse*, but rather the change occurs by a process that seemingly proceeds from numerous centers within the old crystals. The phenomena observed in Fig. 44,[1] though actually showing a
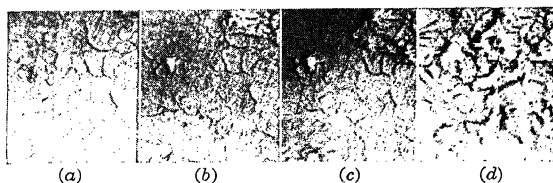
Fig. 44.—Four "frames" of a film showing the transformation (surface) changes in iron at 904°C.   (*Rogers and van Wert.*)

change on heating, appear to lend credence to this notion.   The photomicrographs are four somewhat separated "scenes" (frames) from a continuous film, showing the polymorphic transformation of alpha iron into the gamma modification that occurs, on heating, in the vicinity of 904°C.   The first "scene" (a) shows grains of alpha iron covering the whole field, except the extreme right-hand corner of the frame where some transformation to the high-temperature gamma form has already taken place.   This change is evident by the slight roughening of the hitherto smoothly polished surface of the specimen in that particular corner, a condition brought about by reason of a volume change occurring when the body-centered form passes into the face-centered one.   The wrinkling of the earth's crust by the geological processes responsible for mountain forming is an analogous phenomenon.   In (b), a "scene" taken a fraction of a second later than (a), the area occupied by the transformed gamma phase is larger, and also, a new gamma area near the left-hand edge of the frame has now put in its appearance.   Photographs (c) and (d) show still later (by a second or two) "scenes" in the episode, where further progress

[1] From a film "Surface Changes in Some Metals at High Temperatures," by Rogers and van Wert (1931).

in the transformation has been made. Examination of the continuous film, projected at the speed at which the film was taken, reveals a continuous progress of the change from what appear to be different centers within the parent matrix.

The final grain size of wrought (worked) metal is determined otherwise than by the freezing rate of the metal. This matter is pertinent in another connection, and for that reason a detailed consideration of the subject is reserved till we discuss, in the last chapter, annealing effects on the properties, including grain size, of cold-worked metal. When a metal (or alloy) is inelastically deformed and permanent "set" occurs, the several grains of the metal matrix become fragmented and distorted. This fragmentation and distortion result from an intracrystalline movement of portions or "blocks" of the individual crystals over one another, seemingly in an effort, on the part of the crystal, to forestall rupture. Thus, *plastic flow* in the crystalline metals takes place by "slip" mainly within the constituent crystallites. This manner of plastic flow quite

Fig. 45.—A very low carbon steel. Cold-rolled to 50 per cent reduction. 100 ×.

naturally affects the micro-appearance of the grains, and two photomicrographs of cold-worked metal are reproduced here for what interest they may have. A photomicrograph of cold-rolled (to some 50 per cent reduction in thickness) metal is shown in Fig. 45; the deformation (elongation) of the individual crystalline units is patent enough, but the actual granular fragmentation is, however, not shown at this low magnification (100 ×). If this cold-worked crystalline mass, whose individual units have become crumbled and misshaped, is heated at the proper temperature for a sufficient length of time, an entirely new set of crystals— quite strain-free, whole, and of normal shape—replaces the old distorted and shattered ones. In other words, a proper annealing causes the strained crystallites to *recrystallize*.

And, perhaps what is equally significant, the newly formed crystals reveal—under some circumstance, too eagerly, one

might add—the largely hitherto, latent powers of crystal growth. This particular attribute of a crystal, so passive and unobtrusive in the strain-free crystal that its possession may have been quite unsuspected, now actively asserts itself, and the little recrystallized units of the annealed metal grow vigorously, and to such dimensions as time, temperature, and other conditions permit. The difference in the grain size of the specimens whose photomicrographs are shown in Figs. 40*a* and *b* is the result solely of a difference of some 225°C. in the temperature of annealing of two pieces of metal, cold-worked previously to the same amount. The time of annealing was, of course, the same in the two instances. The series of photomicrographs in the series of Fig. 165 shows the effect of annealing temperatures on the grain size of a previously deformed solid solution (of zinc in copper).

Figures 41*b* and 42 illustrate the effect on grain size of a variation in the time factor, of annealing (8 hr. vs. 1 hr. at 875°C.).

The marked grain-size contrast found in the sample of iron photographed in Fig. 41*a* arises from the circumstance that the iron was deformed, previous to the heating, in a rather non-uniform manner, producing within the metal, a "strain-gradient"; this circumstance, with a critical annealing temperature, frequently results in an abnormal disparity in the size of the grains of a metal thus treated. The important matter of abnormal grain growth in cold-worked metal will claim its share of attention during the consideration of general annealing effects in the last chapter.

Finally, we should note another dimensional characteristic of metallic aggregates: The dimensions of the individual crystallites are, in general, the same in all directions, or as it is usually stated, the grains are *equi-axed*. Equi-axiation may be considered, then, the normal condition of the crystalline grains of a metal, and where this condition does not prevail, as in the samples photographed in Figs. 41*a* and 45, one should suspect unusual and disturbing circumstances to have intervened.

The axial-length characteristics of allotriomorphic grains are, of course, dependent on the *shape* of the grains. The shape, in turn, is determined largely, though probably not wholly, by the mutual interference of crystal growth from uniformly distributed centers of crystallization. In a few instances, it has been found possible to disintegrate polycrystalline metal

aggregates in such a way that the individual crystallites can be separated undamaged and in their entirety. An examination of these grains shows a predominance of pentagonal dodecahedra, *i.e.,* twelve-faced cells with each face five-sided. From theoretical considerations, the tetrakaidecahedral cell (a fourteen-walled cell, with eight walls hexagonally shaped and the remaining six walls quadrilaterally shaped) seems "the most general solution of the homogeneous partitioning of space" (Desch), but a study of foam cells, which are perhaps the closest approximation to this ideal cell, shows a general distribution of faces similar to that shown by the crystallites from the disintegrated metals, *i.e.,* the five-sided faces occur most frequently while the four- and the six-sided faces demanded by the theoretical tetrakaidecahedral cell are next in order of frequency.

Grain Boundaries.—In the photographs of the pure metals and of polyhedral solid solutions, it is evident that some sort of boundaries demark the limits of the individual grains. Because the grains are in reality three-dimensional units, the boundaries are enclosing films or envelopes. Whether the boundaries are something more than simple discontinuities between two differently oriented lattices of contiguous units remains to be proved. It seems likely, however, that they are true boundaries. If the boundaries which one sees have substance as well as form, interest centers naturally in just what is "in" the boundary spaces. One explanation of the origin and character of the grain boundary given some years ago[1] postulated that the boundaries consisted of unorganized, *i.e.,* isotropic, metallic matter, the then called vitreous or amorphous cement. This vitreous cement assumedly was uncrystallized metal, that is metal that had become rigid for the same reason that glass becomes rigid, *viz.,* by undercooling and not by actually crystallizing. The explanation of the supposed failure of the boundary metal to crystallize was an ingenious one, but one which modern X ray methods have shown to be inoperative. The explanation was that the last bit of still liquid metal situated between the crystallizing surfaces of two neighboring crystallites is acted upon simultaneously by the crystallizing forces of two differently oriented grains, with each grain trying to pull the liquid into, and to make it conform with, its own particularly oriented

[1] ROSENHAIN and EWING, *J. Inst. Met.,* **8,** 149 (1912).

lattice, with the result that neither succeeds and the residual metal, finding itself unable to do the one thing or the other, does nothing. It remains essentially a liquid—an undercooled, extremely viscous liquid.

There are certain peculiarities of metallic behavior that lend credence to this novel hypothesis, but recent work indicates that

"the atomic attraction is very weak at more than one interatomic distance and practically insensible at a distance of two atomic radii, (so) it is unlikely that liquid molecules, trapped between two growing crystals, would be so equally attracted by them as to remain in a random arrangement rather than attach themselves to either of the neighboring lattices." (Desch.)

An interesting speculation by Gough[1] postulates the presence of truly crystalline matter in the intergranular spaces whose orientation changes continuously, or in small gradations, from that of the one to that of the other contiguous grain. He would thus assign to this crystallized intergranular metal a sort of mosaic structure, but one which is quite patently purposeful since the departure of the atoms on the lattice from strict parallelism provides a "bond" between two distinctly differently oriented crystallites.

SOLID SOLUTIONS

a. The Substitutional Type of Solid Solution.—Any really adequate notion as to what constitutes the metallic state must, of course, be sufficiently catholic to explain the nature, behavior, etc., not only of the elemental metals, but also those of all primary intermetalline phases as the solid solution and the intermetallic compound. These two latter primary alloy constituents may be scarcely less metallic, with respect to any particular essential quality, than the pure metals themselves. We shall, accordingly, begin our discussion of the metallography of solid solutions by making the usual preliminary inquiry into the nature, properties, and kinds of solid solutions.

In a pure metal, all lattice points are occupied by atoms of the metal in question, be that lattice cubic, tetragonal, or hexagonal.[2]

[1] *Trans. Far. Soc.*, November, 1927; see also, Marburg Lecture (1933), before A.S.T.M.

[2] As most of our common metals belong to one of the cubic lattice types, and because of the simpler architecture involved, we shall have this type

In a pure metal A, only A atoms are present and all lattice points are occupied by A atoms. Now, one may ask, what happens when a small amount of metal B, which forms a solid solution with metal A, is alloyed with A. What is the precise mechanism whereby the one metal—metal A, let us say—dissolves the other? The answers to these questions should tell us much about the nature of a solid solution. As a matter of fact, the act of simple or primary solution in the solid state can occur in one of two different ways. The more usual way—the one that may be considered the general case—is for the atoms of B to go into lattice positions normally occupied by the A atoms, by a simple replacement of, or substitution for, the latter. Whereas in the pure metal, A atoms occupied all of the available lattice points, in a solid solution some points are occupied by B. The frequency with which the B atoms occur on A's lattice in the solid solution will depend obviously on the concentration of metal B in the solution. This replacement of A by B atoms takes place in a perfectly random manner; that is, it does in the general case. There is, for example, no apparent preference on the part of the ingoing B atoms as to whether they shall take up corner or center-of-the-face positions in—let us assume—the face-centered lattice of A.

One interesting result of a simple alloying procedure, such as the one described, is the total disappearance of the characteristic lattice structure of metal B, for in the resulting solid solution only A's lattice is found. This circumstance provides us with a convenient way of distinguishing between the solvent and the solute of a solid solution. The solvent metal is commonly considered the one whose lattice survives the alloying process, in the case cited, metal A. Metal B becomes then the solute metal. The basic lattice of a solid solution, *i.e.*, the lattice of the solvent metal, is called the *host* lattice, and the solute atoms on that lattice are known as the *stranger* atoms. For obvious reasons the solid solution itself is called the *substitutional* type of solid solution.

The presence of stranger atoms randomly resident on a host lattice is naturally not without some modifying effect on the

particularly in mind whenever lattice structures are mentioned in the discussion that follows. Yet what shall be said specifically of this lattice is generally equally applicable to the other two less simple metal lattice types.

properties of the lattice and, in consequence, on the properties of the crystal itself. The solute atom, in going into a lattice not its own, surrenders none of its own intrinsic properties; it retains, as far as one can tell, all of its peculiar dimensional and mass characteristics such as atomic radius, volume, mass, etc. Moreover, it is in full possession of whatever forces an atom is normally free to exert upon neighboring atoms of its own or of another species. Quite expectedly then, a crystal whose lattice is tenanted by two different atom species will have some different properties from a crystal of the same basic lattice but whose points are occupied by atoms all of one kind.

The *strength properties* are one group of properties that are affected by solid-solution formation—they are, in general, improved. Solid solutions are definitely harder and stronger than one, and perhaps both, of the two component metals of the solution, the maximum hardness and strength occurring around equi-atomic concentration of the two metals (see Fig. 46). It has been suggested (Tammann) that the better strength properties of solid solutions are the result of the greater mutual attraction of unlike atoms than of like atoms; that is to say, that it is simply a matter of a stronger and more cohesive lattice bond in solid solutions than that which is found in the pure metals. On the other hand, the superior strength properties of solid solutions have been explained (Rosenhain) by an assumed distortion of the host lattice wrought by the presence on that lattice of some atoms of a size different from those normally there. It is known that the presence of stranger atoms does actually change the parameter of the host lattice, and that the change seems to be a function of the concentration of the solute (see Figs. 47 and 48). It is entirely conceivable that the effect of an individual stranger atom on its neighbors decreases with distance, those near being influenced most; these host atoms are the ones that are pulled (or pushed) farthest out of their

FIG. 46.—Hardness of copper-nickel alloys.

equilibrium positions on the lattice, whereas those atoms at some distance are scarcely affected. This results, obviously, in a "warping" of the normally straight and even atomic planes of the lattice, and in a distortion of the lattice as a whole. Defor-mation of such a lattice is, as a consequence, less easily secured. Whichever expla-nation is acceptable, the fact is that the better strength prop-erties of solid solutions are the result of a greater resistance offered to slip in this class of metallic substances than obtains for the simple metals; but whether this increased resist-ance is a consequence of stronger atomic forces acting, as the first explanation states, or whether, according to the second, intracrystalline slip is

Fig. 47.—Lattice constants (para-meters) of the Ni-Cu, Pd-Ag, Au-Cu, Au-Pd, Au-Pt and Au-Ag systems. (*After Stenzel and Weerts.*)

simply mechanically impeded because of the want of a perfect alignment of the atomic strata, one cannot be so sure.

A second consequence of solid-solution formation is a marked increase in electrical resistance of the solid solution as compared
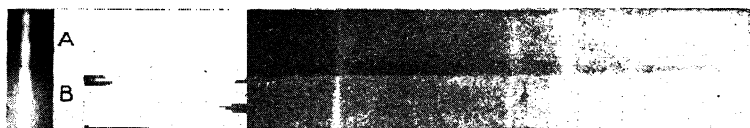
Fig. 48.—Diffraction pattern of (*A*) pure copper, and (*B*) copper-nickel-silicon alloy (96 per cent copper). Hull, or Debye and Shearer method. Note that the diffraction "lines" in the alloy are shifted somewhat to the left as compared to the copper standard. This displacement is an indication of the change in the lattice parameter of copper due to the introduction into its lattice of 4 per cent of nickel plus silicon.

to that of either of the two metals concerned. Two examples of this solution effect will suffice. An alloy of copper and nickel, two metals which form substitutional solutions, containing about 55 per cent copper, has an electrical resistance of around 30 times that of pure copper and 7 times that of pure nickel. Thus copper with its higher electrical conductivity actually

lowers the conductivity of nickel when dissolved in nickel. The effect of additions of zinc to copper, within the range where zinc and copper form a simple substitutional type of solution, is shown in Table 8.

TABLE 8.—ELECTRICAL CONDUCTIVITY OF THE HIGH COPPER COPPER-ZINC ALLOYS (ALPHA BRASS)

Weight of Zinc, Per Cent	Specific Electrical Conductivity
0.00	63.10
0.71	54.56
1.56	46.88
3.07	42.16
5.51	33.22
9.08	27.49
18.02	21.00
20.29	19.75

It is interesting to observe that the effect on conductivity of a given weight of solute differs with the concentration of the solid solution, this effect being the greater in the dilute solutions.
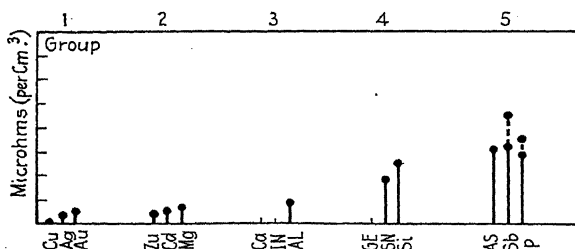
FIG. 49.—Relative increase in resistance caused by 1 atomic per cent of various metals in copper.   (*After Hume-Rothery.*)[1]

For example, in the solution range from zero to 0.71 per cent zinc, the mean depressing effect on conductivity is 19 per cent per each per cent of solute added, while in the more concentrated range of 18 to 20 per cent of solute it is 7.4 per cent.

The magnitude of the lowering effect on conductivity is apparently not independent of the nature of the solute atom. In Fig. 49 (after Hume-Rothery) is given the relative increase in the resistance of copper due to solution of 1 atomic per cent of various metals. The conclusion drawn from the results shown is that the increase in electrical resistance due to the addition of 1 atomic per cent of a solute metal is the larger the

[1] From W. Hume-Rothery's "The Metallic State," Oxford University Press, by permission of the publishers.

greater the distance, both horizontally and vertically, that separates the various solute metals from copper in the periodic table. Thus, the least increased resistance occurs with silver and gold which belong to the same group as does copper; magnesium, zinc, and cadmium of Group II give a somewhat higher resistance; aluminum of Group III still more; and with silicon and tin of Group IV and with arsenic and antimony of Group V the increase is greater still. A similar effect is produced by differences in the vertical distance between copper and the several solute metals. Of the Group I metals, gold has a greater effect on copper conductivity than silver, and of the Group II metals, magnesium has a greater effect than zinc.

It is not readily apparent just why a lattice cohabited by unlike atoms, particularly where the number of the stranger atoms is relatively small, should result in an impairment of conductivity so marked as the cases cited show. Apparently, solid solubility severely limits the movement, or the number, of the electrons responsible for the assumed "electron drift."

Like electrical conductivity, the change in conductivity with temperature (the temperature coefficient of resistance) is commonly much lower for solid solutions than for the pure metals. The changes in this property with increasing concentration of the solute metal are even more pronounced than in the case of conductivity itself. The 55 per cent copper-nickel alloy referred to as having a conductivity of about $\frac{1}{30}$ that of pure copper has a coefficient of resistance of only about $\frac{1}{400}$ that of copper.

The *density* of solid solutions does not differ much from the calculated values; where an appreciable variation from what

TABLE 9.—DENSITIES OF SOME COPPER-ZINC ALLOYS

Weight of zinc, per cent	Observed density	Calculated density
0	8.903	
3	8.892	8.87
5	8.867	8.82
10	8.807	8.72
15	8.745	8.62
20	8.679	8.52

one would expect exists (as in the alpha solutions of aluminum, zinc and tin in copper), the observed density is higher than the values calculated from the rule of mixtures. The densities of some copper-zinc alloys (alpha brasses) are given in Table 10.

b. The Interstitial Type of Solid Solution.—Primary solid-solution formation infrequently occurs in a way whose mechanism is quite different from the one described above. In this second and less common method of solution, the solute atoms take up positions in the interstices or voids of the host lattice but do not actually go on the lattice as happens in the first type. We have in this solution type an instance of what, in effect, is solution by atom addition rather than one by atom replacement, yet as in the substitutional type of solution, the stranger atoms become part and parcel of the host lattice structure. These solid solutions are known as *interstitial* solutions, and they may form whenever the solute atom is relatively much smaller than the atom of the solvent metal. Such a case is the solid solution of carbon in iron. As one might expect from our knowledge of the properties of the substitutional solution, the entrance interstitially of foreign atoms into the lattice of a host metal is of some effect on the properties of the latter; the effects in the two cases are in general similar in that the same properties (density, electrical conductivity, strength properties, etc.) are involved.

The comparative smallness of the solute atom, or the fact of their off-lattice position, or perhaps a combination of the two circumstances, probably accounts for the observed greater rate of diffusion in interstitial solid solutions than is found in the other type. This is rather surprising in view of the generally much lower solubility ranges found in interstitial solutions, for obviously an atom to diffuse must be in solution. In alpha iron, where the solubility of carbon does not exceed 0.035 per cent at 700°C. and is less than 0.01 per cent at room temperatures, carbon diffusion occurs readily at 630°C.

There are a large number of examples of substitutional solid solution among the industrial alloys. Indeed, most of our more important alloys are of this class. Mention has already been made of the high copper copper-zinc alloys, the brasses, in which the face-centered cubic lattice of copper forms the basic lattice. Sister alloys, also substitutional solutions, are the high copper alloys of tin (bronzes) and with aluminum (aluminum bronzes).

In addition to the simple binary alloys of copper, there are a large group of ternary alloys where a third metal is present. We have then three different kinds of atoms resident on the basic lattice. One such alloy is a copper-zinc-nickel alloy known as nickel silver. The very important aluminum-rich alloys containing copper or zinc are also examples of solid solutions of the substitutional type where copper (or zinc) atoms occupy definite points on the face-centered aluminum lattice. Typical alloys of the interstitial type of solid solutions are those of carbon, nitrogen, and hydrogen with iron. The iron-rich quaternary alloys of iron-nickel-chromium-carbon (the stainless steels) are examples of alloys where both modes of solid-solution formation occur in one and the same alloy. The nickel and chromium atoms occupy lattice points on the basic (iron) lattice, replacing iron atoms thereon, while the carbon atoms are interstitially positioned. The photomicrographs of several of these solid-solution alloys are given in Figs. 50 to 52.

Primary and Secondary Solid Solutions.—The substitutional and the interstitial types of solid solutions possess a common character: Each derives its basic lattice from one of the metals involved in solution, to which metal are assigned the name and attributes of the solvent of the solution. Solid solutions in which the lattice of at least one metal concerned survives the alloying process are known as primary solutions. All of the solid solutions mentioned in the preceding paragraphs are primary solid solutions. Each has for its basic lattice the lattice of one (the major) constituent metal. There are binary solid solutions, however, whose lattice structure differs from that of either metal, and these are known as secondary solid solutions.

If we turn back to Chap III, we shall find that in the type equilibrium diagrams described there were at the most but two solid solutions in any particular system. Both were primary solutions, the alpha solution, an M-rich solution with metal M's lattice as its basic lattice, and the beta solution correspondingly related to metal N. Some of these type diagrams admit of expansion so as to include more than two solutions, as, for instance, the diagram of the Group IIIa alloys (page 69). In the Group IIIa diagram, the second (β) solution originates as the result of a peritectic reaction between the initially formed alpha solution and the melt. It is possible to introduce a second

peritectic reaction in the series where pro-peritectic solid β reacts with the melt to form a third solution, which is commonly designated by the third letter of the Greek alphabet, γ. This possibility can be still further extended so as to produce other solutions, as δ, ϵ, η, etc. In the copper-zinc system (also the copper-tin, copper-aluminum, etc.), there are actually five or six of these solutions.

A trisolution peritectic series is given in Fig. 49a, which is, as one can see, simply an extension of the bisolution series of Group IIIa.
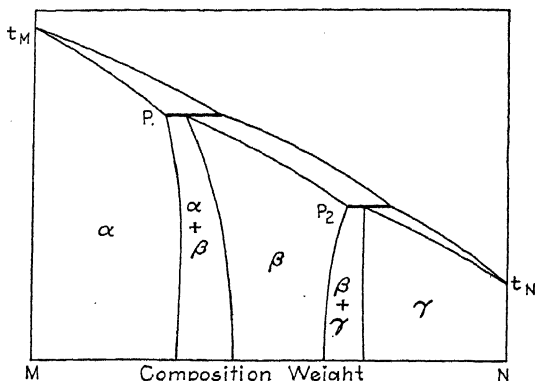
FIG. 49a.—Modification of type equilibrium diagram of Group IIIa alloys.

The two solutions at the end, the terminal solid solutions alpha and gamma, are primary solutions; that is, each has the distinctive lattice of its major metal. The intermediate solution has a lattice that differs from that of either metal M or N. It is by definition a secondary solid solution. In the copper-zinc system (see Fig. 37), the alpha solution has the face-centered lattice of copper, the eta solution at the zinc end of the series has the hexagonal lattice of zinc, while the beta solution, the first of the four intermediate phases, has a body-centered cubic lattice.

Secondary solid solutions are interesting metallographic entities; many of them are structurally complex and (with the inter-metallic compounds) belong to that group of metallic materials whose nature and character are yet largely enigmas. Some of the secondary solutions, notably the beta solutions of the copper systems, are rather metal-like in their properties; they are, for example, only a little less plastic and tough than the alpha solu-

tions, or even than copper itself. But others of their kind depart far from real "metallicity," they are poor conductors of heat and electricity and they are notoriously brittle. The gamma solutions of some copper systems afford instances of secondary solutions which definitely lack many of the common metal properties. They resemble the intermetallic compound group of metallic substances which, too, are characterized by a want of toughness and which possess a relatively high electrical and thermal resistance. The absence of well-developed plastic properties in these secondary solutions is properly ascribed to their complexity. The quasimetallic gamma solutions of the copper series referred to have a unit cell of 52 atoms, which can be distributed obviously in no simple fashion.

Fig. 49b.—Electrical resistance of the copper-palladium series. The full line is the resistance of non-symmetrical solutions, the broken line is that of the symmetrical solutions in the neighborhood of 75 atomic per cent copper. (*After Hume-Rothery.*)[1]

Symmetrical Solid Solutions. It has been stated that in the general substitutional type of solid solution the solute atoms are distributed in a perfectly random and irregular manner. This absolutely indifferent attitude on the part of the ingoing solute atom in the matter of where it shall abide on the host lattice is all but universally true. Some exceptions, however, have been observed. One flagrant—though not the only violation of the general rule of random distribution of solute and solvent atoms on the basic lattice—is afforded by the copper-palladium alloys. This is a normal substitutional type of solution series, and under the usual homogeneization (annealing) treatment any alloy of the series will show the copper and the palladium atoms randomly distributed with respect to one another; that is, each atom's place on the lattice is determined solely by chance. But if certain alloys of this series, specifically those in which the ratio of the number of atoms of the two metals

[1] From W. Hume-Rothery's "The Metallic State," Oxford University Press, by permission of the publishers.

is a small whole number—as, for example, the 75 atomic per cent copper alloy—are annealed for a long time, it is found that the
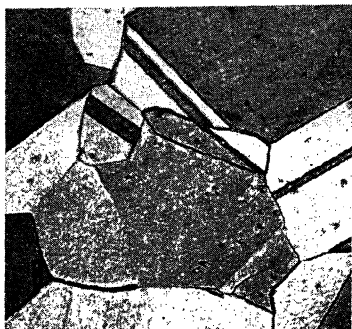
FIG. 50.—Copper-zinc alloy (70 per cent copper). 100 ×. (*Photograph by students in Harvard Metallurgical Laboratories.*)
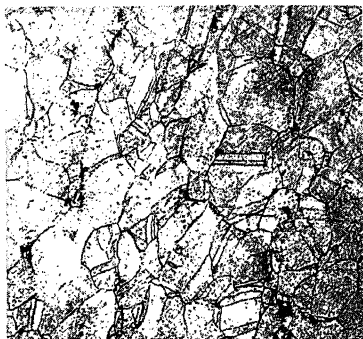
FIG. 51a.—Copper-nickel-zinc alloy (nickel silver). Cu = 55 per cent, Zn = 25 per cent, Ni = 20 per cent. 100 ×. (*Photograph by students in Harvard Metallurgical Laboratories.*)

randomly positioned arrangement of the two atomic species no longer exists, for the palladium atoms are, for the most part, now

FIG. 51b.—Copper-zinc-tin alloy, showing three microconstituents, all solid solutions. The twinned constituent is the ternary alpha solution, the gray areas outlined in white are the beta solution, and the white edging is the delta. 1000 ×. (*Photograph by Wilson.*)

located at the cube corners and the copper atoms are generally concentrated in the center-of-face positions. This variant of the

general case is known as a symmetrical solid solution, sometimes referred to as a superstructure.
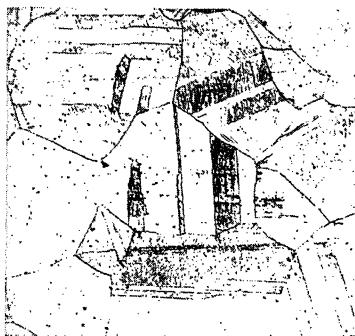
FIG. 52a.—Iron-chromium-nickel-carbon alloy (stainless steel). Nominally, 18 per cent Cr, 8 per cent Ni, 0.03 per cent C, and the remainder Fe (gamma). 100×. (*Photograph by students in Harvard Metallurgical Laboratories.*)

FIG. 52b.—Silver-indium alloy (4 per cent indium). 100×. (*Photograph by Jarrett.*)

Superstructures can occur also in secondary solid solutions. In the copper-zinc alloys containing the beta solution (43 to 61 per cent copper), the change $(\beta \rightleftharpoons \beta')$ at 470° to 453°C. is known to be associated with the development of a symmetrical beta solution (called the β'-solution) on cooling, and the reverse change on heating.

The exothermic nature of the $\beta-\beta'$ change indicates that the internal energy of the symmetrical solution is less than that of the solution in which fortuitous distribution prevails. The electrical resistance is also lowered by the assumption of a symmetrical arrangement (see Fig. 49b).

FIG. 52c.—Iron-columbium (nio- 1 per cent Cb.

Microstructure of Solid Solutions. *a. The Homogeneized Solid Solution.*—When, by a suitable thermal treatment, all

original inequalities in composition existing in the alloy by reason of selective freezing have been corrected, the microstructure of a solid solution does not differ essentially from that of a pure metal. Photomicrographs of several homogenized solid solutions are given in Figs. 50 to 53. All show the polyhedral or network structure that we have learned to associate with the micro-appearance of the pure metals. In Fig. 50 (also Fig. 14b), we have the microstructure of a copper-zinc alloy (alpha brass) containing 70 per cent copper. This is a representative solid solution of the substitutional type with copper as the host lattice. In general micro-appearance the structure is not unlike that of copper. The color of the alloy is, of course, yellow, whereas copper would be reddish. A difference in etching attack, the result itself of a difference in orientation, accounts for the difference in shading of the grains from light to almost black. Color differences are again not due to varying chemical composition between the constituent crystallites, for all are chemically identical. A microfeature not found in the structure of the body-centered iron is found here. Many of the grains show quadrilateral areas extending across the grain. These portions are bounded by perfectly parallel sides, and the portion of the grain enclosed within the area is shaded differently from the remainder of the grain. Evidently, orientation differences between the two parts are responsible for the difference in etching effects. We have here what crystallographers call a *twinned* crystal, and the two portions of the crystal—the twins—are rotated exactly 180 deg. to one another. Twinning of this type is common in metals and alloys which have a face-centered cubic lattice and which have been annealed subsequently to straining. Profuse twinning is shown also in the silver-indium alloy (Fig. 52b). The microstructure of a ternary solid solution (primary) of the substitutional type (zinc and nickel in copper) is shown in Fig. 51a. This alloy, owing to its lower copper content and to the superior "whitening power" of nickel, is silvery white in color. Twinning is in evidence. Another ternary alloy, but this one consisting of three distinct microconstituents, is shown in Fig. 51b. Figure 52a shows the microstructure of a quaternary alloy.

Figure 53 gives the structure of a secondary solid solution; it is the beta solution of the copper-zinc series. Note the large untwinned grains. In the next illustration (Fig. 54) we have

both a primary and a secondary solid solution in the same alloy, the alpha (dark) and the beta solution in a 60 per cent copper brass, and in Fig. 55 the corresponding alpha and delta
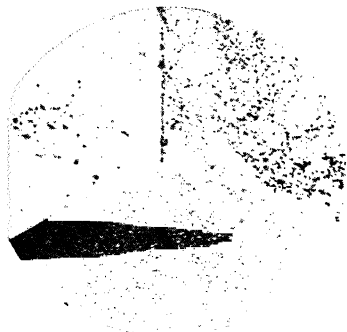
FIG. 53.—Copper-zinc alloy (52 per cent Cu). Beta brass. 100×. (*Photograph by students in Harvard Metallurgical Laboratories.*)

FIG. 54.—Copper-zinc alloy (60 per cent Cu). Alpha and beta (light) solutions. 100×. (*Photograph by students in Harvard Metallurgical Laboratories.*)

solutions of the copper-tin series. Figure 52c gives the photomicrograph of a primary solid solution of two body-centered cubic metals, iron and columbium.
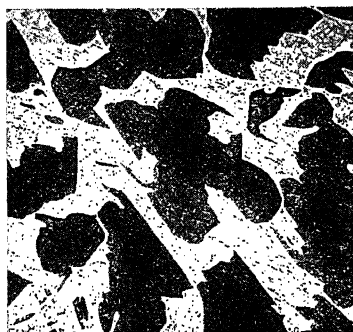
FIG. 55.—Copper-tin alloy (80 per cent Cu). Alpha and delta (light) solutions. 100×. (*Photograph by students in Harvard Metallurgical Laboratories.*)

FIG. 56.—Copper-silver alloy (cast). 100×. (*Photograph by students in Harvard Metallurgical Laboratories.*)

b. The Unhomogeneized (Dendritic) Solid Solution.—The characteristic microfeature of a fully homogeneized solid solution is

the presence of definite and well-defined polyhedral crystalline grains, randomly oriented. This is not the initial condition of the alloy, as originally cast, but a condition that has been brought about by a proper sequence of mechanical and heat-treating operations. The original, cast structure of solid solutions is quite another story from that told by the foregoing photomicrographs. In Figs. 56 to 62 are shown seven photomicrographs of cast alloys, and the peculiar structure there exhibited is known as the *dendritic* (treelike) structure. The individual units (as in Fig. 57)
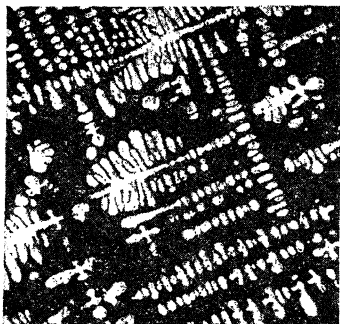
FIG. 57.—Aluminum-silicon-sodium alloy. Dendrites of an aluminum-silicon solid solution in an eutectic matrix. 50 ×. (*Photograph by students in Harvard Metallurgical Laboratories.*)

FIG. 58.—Same as Fig. 57, but showing the eutectic resolved. 500 ×. (*Photograph by students in Harvard Metallurgical Laboratories.*)

are called *dendrites*. It will be observed that the polyhedral granular structure of pure metals and of homogeneized solutions is absent.

The formation of the somewhat fantastically appearing dendrites in a solid solution is a consequence of the particular, *i.e.*, selective, manner of freezing of these substances, of which we learned in Chap. III. When a molten metal or alloy is slowly cooled to its freezing point, solidification begins at various centers in the melt; the freezing process then continues to completion with deposition of more solid (crystallized) matter on the nuclear crystals: in other words, the initial nuclei grow by accretion. This accretive growth, however, is not uniform. Each little nuclear crystal grows faster in certain directions than in others, with the three principal axial directions as the preferred directions

of growth. The ultimate result, with respect to each growing crystalline unit, is the production, first, of a solid dendritic skeleton, followed by the filling in of the skeletal framework. The stages in the formation of such a dendritic crystallite are diagrammatically shown as in Fig. 63. In (*a*) of Fig. 63 is shown an early stage in the development of a dendrite where two major axes (the third being normal to the page surface) are forming from a single nucleus, originally at the intersection of the axes. In (*b*), we have a somewhat later stage in the dendritic development, where growth has enlarged the axes, radially and longitudinally, and where secondary axes, paralleling the major axes, are beginning to form. In (*c*), which represents the

Fig. 59.—Dendritic structure in a cast steel. 0.40 per cent carbon. 100×. (*Photograph by Chow.*)
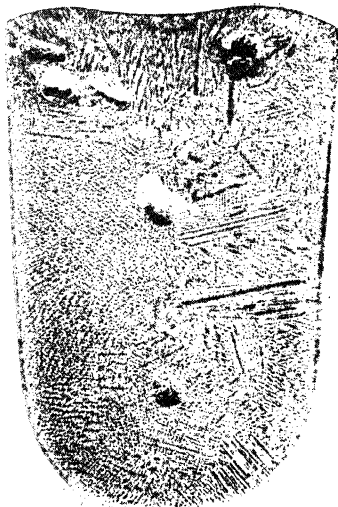
Fig. 60.—Dendritic structure in steel. 0.40 per cent carbon. (*Photograph by Chow.*)

final stage in dendrite formation, occurs the filling up of the interstices between the several axes with more crystalline metal.

In such a manner, pure metals and solid solutions freeze. The resulting solid mass is an aggregate of a great number of juxtapositioned, even interlocking dendritic crystallites, or dendrites. But there is one fundamental difference between dendritic formation in pure metals and in solid-solution alloys. In a pure metal, the several axes—the majors, the various sets of minor axes—and the interstitial metal, the fillings, so-called, are all chemically alike. All are pure metal and nothing else.

In point of time of origin, the various parts of a pure-metal dendrite may differ, but each portion is of a composition identical with every other portion. But because of the selective nature of the freezing mechanism of a solid solution, where the crystallizing solid varies in composition continuously from beginning to end, the first portions of a dendrite to form differ chemically from those forming subsequently. Consequently, and despite diffusion's mitigant effects, a solid-solution dendrite is chemically rather a heterogeneous affair. The major axial portion of such
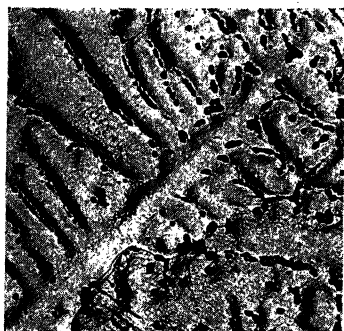
Fig. 61.—Dendritic structure in cast silver-copper alloy (1 per cent silver). 100 ×.
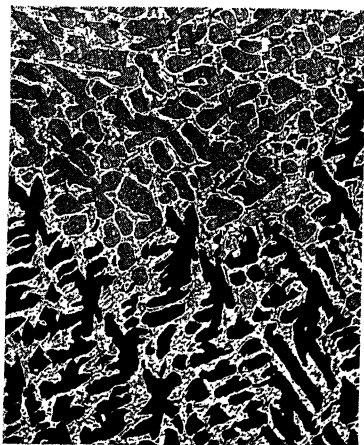
Fig. 62.—Dendritic structure in bronze (20 per cent tin). 100 ×.

a dendrite will differ somewhat chemically[1] from the later forming secondary axes, and these in turn will be different from the finally forming fillings. This sort of heterogeneity is a form of segregation—dendritic segregation, it is called—and is an inevitable concomitant of dendritic formation whenever the separating solid differs in composition from its parent melt.

In cases where restricted solid solubility exists, as in case IIa, the limit of solubility may be reached before dendritic formation is complete; i.e., the latter parts of the dendrite—the fillings—will be occupied by a simple mixture (eutectic). This is the

[1] Comparatively poorer in the element which causes the depression of the freezing point.

condition prevailing in the alloy of Fig. 57. Not only the dendritic fillings, but the general matrix of this alloy is such an eutectic.

The lack of chemical heterogeneity in dendrites of the pure metals precludes the possibility of revealing their dendritic nature by etching methods which depend for their action on differences in composition. In solid-solution dendrites where segregation does occur, dendritic structure is made manifest by etching. Dendritic existence *per se* is not revealable by etching; dendritic segregation is.

A solid-solution dendrite, as the original individual unit of crystalline matter, may (does) of its own accord disintegrate into smaller units—micrograins—by the process known as *granulation,*

(a)   (b)   (c)
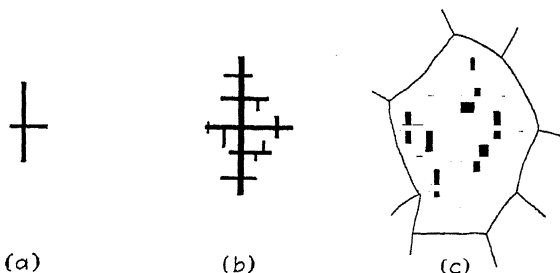
Fig. 63.—Stages (diagrammatic) in the formation of a dendrite.

but the accompanying segregation may not be destroyed so easily. (See Fig. 161.) Annealing at high temperatures, and particularly annealing following cold deformation, may permit diffusion to take place to the extent where little or no chemical inequalities exist. But dendritic segregation is often extremely persistent and its survival after many heat and mechanical treatments is one indication of the tenacity and lastingness of certain effects of some inceptive and early conditions in an alloy's history.

INTERMETALLIC COMPOUNDS

It is perhaps not surprising that the metals should form compounds among themselves, and that these compounds should possess, in general, some of the more characteristic properties of all chemical compounds, as constancy of melting point, definite combining ratios, etc. Two examples of a large number of

intermetallic compounds are copper aluminide, $CuAl_2$, found in the copper-aluminum system, and copper stannide, Cu_3Sn, found in the copper-tin alloys. Another very important compound technically, because it is found in the steels and cast iron, is iron carbide, Fe_3C; it is, however, a compound of a metal with an alloying nonmetal. In these compounds the ordinary rules of valence are violated. This particular nonconformity on the part of intermetallic compounds is a general condition, though exceptions exist; it is an indication that chemical combination among metals is not altogether like the more common kind of chemical union responsible for compounds like sodium chloride, copper sulphate, etc.

The properties of intermetallic compounds are quasimetallic. Usually they are hard and brittle substances, though an accurate evaluation of the strength properties is impossible because of their extreme brittleness. The electrical conduction is uniformly low as compared to the elemental metals. One could rightly expect that the usefulness of intermetallic compounds would be severely limited. Yet in many alloys they are a useful constituent, though rarely are they ever present except in small amounts. When present in limited quantities, they affect (increase) the strength properties, but more often their function is toward a specific purpose, for example, they are the "hardeners" in most age-hardenable alloys, they are the load-bearing and antifriction constituents of some bearing metals, and they act as a mechanical obstruction to grain growth in other alloys.

What few intermetallic compounds have been investigated by X ray diffraction methods have been found to possess a complex fine structure. Ag_3Al and Cu_5Si, for example, have unit cells of 20 atoms each, divided into two groups of 12 and 8 atoms, respectively. We have seen that in a truly nonsymmetrical solid solution the solvent and solute atoms are randomly distributed with respect to one another. In their fine-structural characteristics, intermetallic compounds are somewhere between solid solutions and the "ideal chemical compound" of Westgren's[1] description; they are intermediate in character, for while like atoms may not all be similarly situated, their distribution in the lattice is not determined altogether by chance. But structural intermediacy is not the only indefinite attribute

[1] Westgren and Phragmen, *Phil. Mag.*, **6**, 50, 311 (1925).

of intermetallic compounds; their method of atomic linkage is also apparently a sort of a compromise between two ideal bonding types. And, perhaps, in this circumstance we have our best criterion by which one can judge an intermetallic compound's nature.

On the basis of the modus operandi of the attractive forces acting, there are two distinct kinds of bonding in crystalline substances, two ways by which the constituent atoms of a crystalline solid are held rigidly in a lattice. One of these ways acts essentially through actual transfer of electrons from the one atomic species to the other. This is the manner of bonding found in all common ionic compounds, as, for example, sodium chloride, whose simple cubic lattice was illustrated in Figs. 6 and 7. In this compound, the positive sodium atoms with an electron distribution of 2–8–1, in the first, second, and third rings, respectively, have each a single electron in the outer ring in excess of that required for a symmetrical distribution. This superfluous electron is surrendered to the negative chlorine atom, whose 2–7 electron distribution gives an outer ring that is structurally asymmetrical by a single electron. The cession of one electron by the sodium atom to become a positively charged sodium ion, and the acquisition of an additional electron by the chlorine atom, making it a negatively charged chlorine ion, provide the necessary electrostatic conditions for stable chemical union and for a rigidly bonded crystalline lattice. This *electron-transfer type* is commonly known as the *ionic* or *electrovalent* type. As stated, our common chemical compounds of the sodium chloride type belong here.

The second kind of bonding results from a sharing, rather than from an actual transfer, of electrons by the two kinds of atoms. A certain, identical number of electrons of each of the two atoms concerned participate equally in the union, yet neither the one atom ever relinquishes full ownership of its own electron, nor does the other acquire full possession. This is the *covalent* or *homopolar* type of bonding. The diamond is a typical example of this kind of bond, where each tetravalent carbon atom is surrounded tetrahedrally by four other carbon atoms. While the true homopolar bond produces substances which are quite nonmetallic in character and properties, the "normal metallic kind of linkage"—to use Bernal's phrase—is of this particular

type, but it is a case of imperfect homopolarity, differing from the true type to the extent in which electronic interchange is possible. In the metals of Group I (sodium, potassium, etc.), whose high atomic electrical conductivity definitely stamps them as among the truest metals, the possibility of electron sharing in the homopolar bonded lattice is really quite free and unrestricted. This case represents an extreme variant of true homopolarity. The other extreme is exhibited by the diamond lattice. Here the shared electrons are so firmly held by the participating atoms that, except under high electrical potential when rupture of the linkage may occur, the substance is a nonconductor. While the freedom of interchange of electrons naturally varies with the individual homopolar solid, the comparatively much greater freedom enjoyed by the metals in this matter justifies Bernal's name ("normal metallic kind of linkage").

This brief review of the notions concerning the origin and nature of the forces holding solid substances rigidly together brings us to the point where we can more intelligently discuss the not as yet too well known nature of intermetallic compounds. An intermetallic compound may be defined as an intermediate metallic phase in which chemical combination has taken place, either as the result of electron transfer or of electron sharing. Thus, at the outset, we are confronted with the fact that the causal combining forces in an intermetallic compound may act in one of two ways. These, on the one hand, may operate as in the ionic or saltlike manner when actual electron transfer occurs, or they may achieve a similar result by the atoms merely sharing electrons. This gives us the homopolar or the diamond type of bonded lattice. The quasimetallic character and conduct of intermetallic compounds originate in their assumed possession, in varying degrees, of the metal type of bonding, that is to say, a covalent bond of wide freedom of electron interchange. This is supposed to be true of the basically ionic intermetallic compounds, in which cases some electrons escape actual transference to form a loose covalent tie. However, some of the "metallicity" of ionic intermetallic compounds may arise from the circumstance that the negative ion is not very stable and tends to liberate electrons on provocation. It seems that we must be content, for the present at least, with this highly speculative explanation of the sources of an intermetallic compound's metallic nature and

behavior.   We shall next consider another matter of like obscurity, *viz.*, a metal's valence in its intermetallic compound.

First, concerning the fact itself.   In the chemical compounds which the metals form among themselves, we do not commonly find, as has been noted, that the two metals are united in the proportions that the usual rules of valence prescribe.   One example, already cited, the technically important compound copper aluminide, $CuAl_2$, has one atom of copper combined with two atoms of aluminum to form one molecule of the compound. Now, aluminum has a usual valence of three, which would give copper a valence of six in the compound, whereas, as is well known, copper's valence is either one or two.   Further instances of intermetallic compounds, illustrating similar or even more glaring irregularities in valence relationships, are: Cu_2Zn_3, Cu_3Sn, Mg_2Sn, $AuCu$.   Nonconformity appears to be a rather general occurrence. The reason for this has been given essentially as follows:

. . . the essence of chemical combination (is) that the atoms share or exchange electrons in such a way that stable groupings are formed, and the so-called valency rules of the ordinarily nonmetallic compounds of chemistry are the result of two facts, *viz.*, firstly, that certain definite numbers of electrons constitute stable groups (usually octets), and, secondly, that all the available valency electrons are used up and bound into the stable groups.   It is because all of the valency electrons are employed, that the metallic properties of the constituent elements are lost in the compound.   Consequently, it is at once apparent that, if free electrons are left over so as to make a truly metallic compound, the valency relations must in general be different from those in the normal compound in which all the valency electrons are used up."   (Hume-Rothery, " *The Metallic State*," page 329.)

The use of the novel concept " compounds of variable composition" is an attempt to clarify further the dubious nature of what we have called secondary solid solutions, in particular those secondary solutions in which actual compound molecules, on evidence direct or indirect, appear to be present.   We have defined secondary solutions as intermediate phases of lattice structure unlike either of the participating metals.   In many cases the lattice structure of a solid solution is definitely that of a compound falling within the composition limits of the solution. In other words, these secondary solid solutions are "built around,"

as it were, a definite intermetallic compound whose lattice becomes that of the solid solution. This fact, of course, explains why the secondary solid solution differs structurally from the lattice of pure metals and also why they often resemble intermetallic compounds in properties. These solutions, in keeping with their kind, show a range of composition which may be considerable as is the case of the beta solution in copper alloys. It is to such secondary solid solutions that the term "compounds of variable composition" has been applied.

Interesting and highly evidential as to the electronic character of the bond is the observation made by Hume-Rothery that in the basic compound of certain of these intermediate phases there exists a definite ratio of valency electrons to atoms. For example, in the first of these intermediate phases of some alloys, the beta secondary solid solution, the ratio is $3/2$. In the copper-zinc system, the beta solution ranges around the composition (compound) of equi-atomic per cent, $CuZn$. The number of atoms is two; the valency electrons are two from the divalent zinc and one from the copper, or three in all. The ratio of valency electrons to the number of atoms is thus $3/2$. In the copper-aluminum series, the beta phase hovers around the composition given by the formula Cu_3Al; four atoms and six valency electrons (one for each of the three coppers and three for the trivalent aluminum) are involved, and the above ratio is again $3/2$. In the copper-tin series the basic composition of the beta phase is the composition Cu_5Sn, whose six atoms and nine valence electrons (five from the monovalent copper and four from the tetravalent tin) give again a $3/2$ ratio. The systems silver-magnesium, silver-zinc, gold-zinc, and others exhibit the same occurrence.

In these same alloy systems, another intermediate phase is the gamma solution of a still more complexly structural organization than the beta solutions. Yet a similar relationship between the number of atoms and the valence electrons of the basic composition has been observed, but the ratio is now $21/13$. The fundamental unit of the gamma phase in the copper-zinc and the copper-aluminum series is Cu_5Zn_8 and Cu_9Al_4, respectively, and the ratio of the number of the total valency electrons to atoms is $21/13$ in each case. This particular relationship has been observed also in the gamma phase of the copper-tin, silver-zinc, gold-zinc, and others.

The microstructure of some alloys in which intermetallic compounds occur is shown in Figs. 64 to 69.   In the first of these
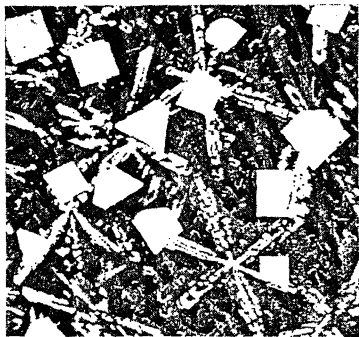
Fig.   64.—Tin-copper-antimony alloy (Babbitt metal) $Cu = 7$ per cent, $Sb = 10$ per cent, $Sn = $ remainder. $50 \times$.   (*Photograph by Farrar.*)
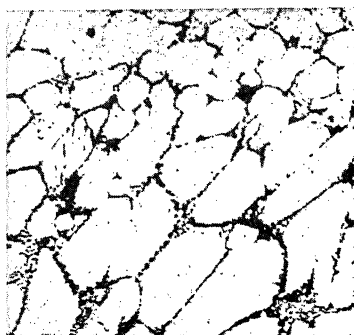
Fig.   65.—Fe_2As (white)   and eutectic network of compound and iron-arsenic solid solution.   Analysis: 36 per cent As, 1.3 per cent Pb, remainder Fe. $100 \times$.   (*Photograph by Greene.*)

(Fig. 64), which is the microstructure of a tin-copper-antimony alloy, are two compounds.   The radial crystallites are the compound Cu_3Sn, and the square or triangular shaped (idiomorphic) crystallites are the compound $SbSn$.   The matrix of the alloy is a tin-rich solid solution.   A number of photomicrographs (Figs. 65 to 69) show microstructures of compounds occurring in copper, lead, arsenic, iron, and antimony alloys.   Further discussion of the microstructure of intermetallic compounds is given below.

Segregate and Other Duplex Microstructures.—Our study of equilibrium diagrams showed that alloys may consist, at ordi-

Fig. 66.—Cu_3Sb (dark) and Cu_2Sb (light). $100 \times$.   (*Photograph by Greene.*)

nary temperatures, of more than one phase, and in some of the photomicrographs already given more than one microconstituent has been present.   The duplex structure of many alloys results from

the particular method of freezing, as is the case in a eutectiferous series.   In other alloys, it is the consequence of changes that occur in the solid alloy as, for example, when an eutectoid inversion

Fig. 67.—Antimony crystals (light), Cu₂Sb (gray) and dark eutectic matrix. 100 ×.   (*Photograph by Greene.*)

occurs.   In still others, a duplex structure originates when a phase is precipitated from a supersaturated solid solution.   The

Fig. 68.—Dendritic forms are sulphides (dark) and arsenides (light).   100 ×.   (*Photograph by Greene.*)
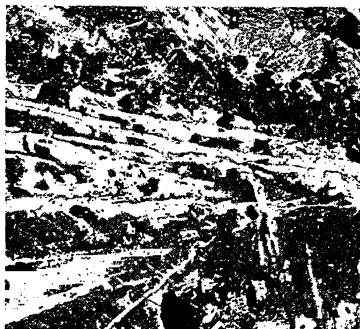
Fig. 69.—Fe₂As (white blades) with ground mass of Cu₃As principally, in copper-arsenic-iron alloy. 100 ×.   (*Photograph by Greene.*)

precise manner of distribution and the metallographic character of the two (or more) phases depend largely on the conditions under which the phase is formed as, for example, the rate of

cooling and the total composition of the alloy and—when a phase is derived from a preexisting solid phase—the crystallographic properties of the separating and the parent phases. One may make the following convenient classification of duplex alloy structures, though with respect to origin and form all classes named are not wholly dissimilar: (*a*) eutectic and eutectoid structures, (*b*) Widmanstätten structures, (*c*) the martensitic structure, and (*d*) intra- and intergranular segregates (inclusions).

a. Eutectic and Eutectoid Structures.—The origin of these metallographic forms has already been discussed. The first is the
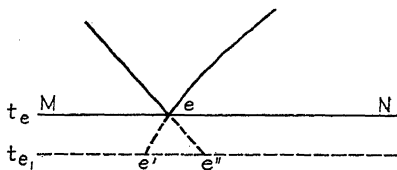
Fig. 70.—Diagrammatic representation of a possible way eutectic aggregates may form.

(Undercooling lowers the temperature of the melt from the true eutectic temperature t_e to a slightly lower temperature t_{e_1}. The melt becomes thereby supersaturated with both metals. The metal of higher nuclei number—say, metal *M*—will start the crystallization process off. The growth of the initial *M* crystals proceeds but a little way, however, when nucleation of *N* becomes active. Crystallites of *N* grow meanwhile to appreciable dimensions. The precipitation of solid *M* and *N* changes the condition of the residual melt from one of supersaturation to one of simple saturation. Slight undercooling is necessary to bring about a repetition of the cycle).

result of a simultaneous precipitation at constant temperature of two solid phases from a liquid solution; the second is a consequence of an analogous biphasial precipitation from an already existing solid solution. The microstructures of some typical eutectics are given in Figs. 71 to 78. No detailed descriptions of these will be attempted. One should, however, examine each photograph carefully. It should be noted that, while considerable diversity in micro-appearance prevails, eutectics are most often made up of alternate, roughly curvifoliate laminae of the two phases. This laminated structure originates probably in some such manner as is described in Fig. 70.

In alloys whose composition falls exactly at eutectic proportions the microstructure of the alloy is 100 per cent eutectic (see Fig.

72); alloys whose total compositions are to either side will have excess constituent in addition to the eutectic. Since the eutectic forms (freezes) last on cooling, it is found in the dendritic fillings (Fig. 75) or around the polyhedral grains (Fig. 76).
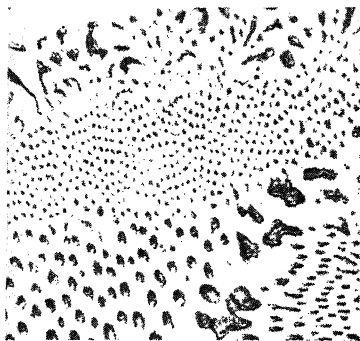
Fig. 71.—Eutectic in iron-arsenic alloy (75 per cent Fe). 110×. (*Photograph by Greene.*)
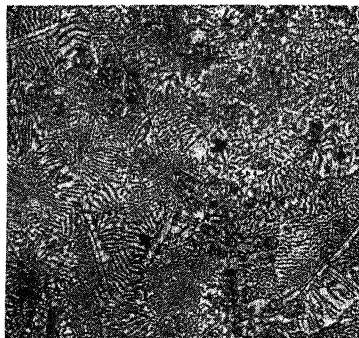
Fig. 72.—Eutectic of PbS-Cu$_2$S, in copper-lead-sulphur alloy (50 per cent Cu and 32 per cent Pb) 100×. (*Photograph by Greene.*)

Fig. 73.—Eutectic in copper-antimony alloy. 100×. (*Photograph by Greene.*)
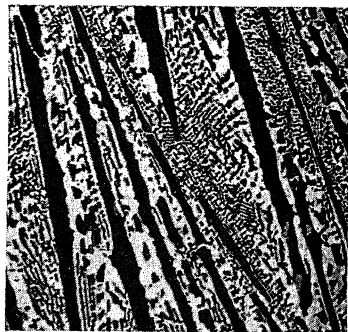
Fig. 74.—Eutectic of copper-antimony solid solution and Cu$_2$Sb in copper-antimony alloy. 100×. (*Photograph by Greene.*)

Three photomicrographs of an eutectoid (pearlite) found in iron-carbon alloys are given in Figs. 79 and 80. Their micro-appearance justifies the name eutectoid (eutectic-like). Pearlite forms, as we remember, as the result of an eutectoid inversion at about 0.90 per cent carbon and around 700°C.

The properties of these aggregates are considered in the next chapter.

b. The Widmanstätten Structure.[1]—When a phase or other change in the solid state results in the creation of a new phase,
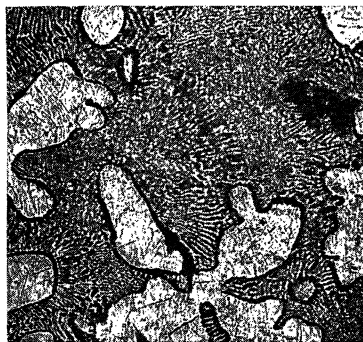
FIG. 75.—Crystallites of Cu₂S in copper-sulphide–lead-sulphide eutectic. 100×. (*Photograph by Greene.*)
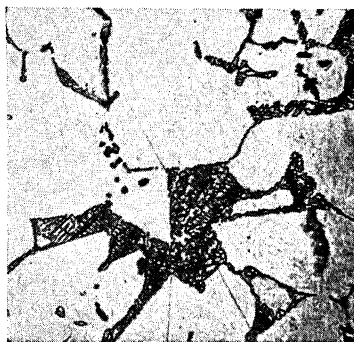
FIG. 76.—Eutectic fillings of copper-antimony solid solution and Cu₂Sb. About 15 per cent Cu. 100×. (*Photograph by Greene.*)
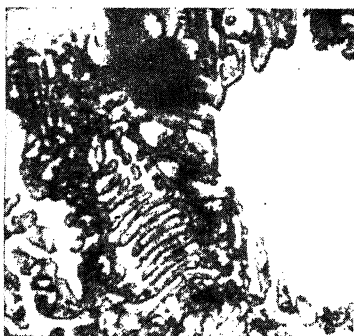
FIG. 77.—Same as Fig. 76. 1000×. (*Photograph by Greene.*)

FIG. 78.—Eutectic in iron-tungsten-vanadium-carbon alloy (high-speed steel). 500×. (*Photograph by Reed.*)

the latter's separation from the parent phase may occur principally along the crystallite. boundaries, in which case one gets an accentuated polyhedral or network pattern. Or the separation

[1] Named after von Widmanstätten, who first observed the structure in meteorites (see Fig. 88).

may take place, for the most part, actually within the crystallites, preferentially along certain crystallographic planes.   The practical consequence of such a localized intracrystalline segregation of the derived phase is, obviously, to give the segregate a definite orientation with respect to the parent, and to produce in the etched alloy a characteristic microstructure known as the cleavage

FIG. 79.—Eutectoid (pearlite) in an 0.87 per cent carbon steel.   500 ×. (*Photograph by Reed.*)

FIG. 80.—Eutectoid (pearlite) in an 0.87 per cent carbon steel.   500 ×. (*Photograph by Reed.*)

or Widmanstätten pattern.   The particular plane (or planes) of the lattice of the parent along which the derived phase chooses to precipitate is manifestly of some interest.   It is commonly a closely packed plane, which is determined, apparently, by the circumstance of its approximate coincidence with a similarly packed plane of the precipitating phase.   For face-centered cubic parent structures, the favored precipitating plane is the octahedral plane, the (111) plane, for it so happens that it is this plane of this lattice set-up which is most nearly coincident with,

for example, the densely packed (110) plane of a body- or face-centered cubic precipitant, or the basal plane of a hexagonal close-packed precipitant.

Preferred precipitation along the octahedral planes explains the frequency of occurrence of 60-deg. angles in the Widmanstätten

(a) *The copper-rich precipitate forms along the {111} planes of the silver-rich parent solid solution.*

(b) *The silver-rich precipitar forms along the {100} plane of the copper-rich parent solid solution*
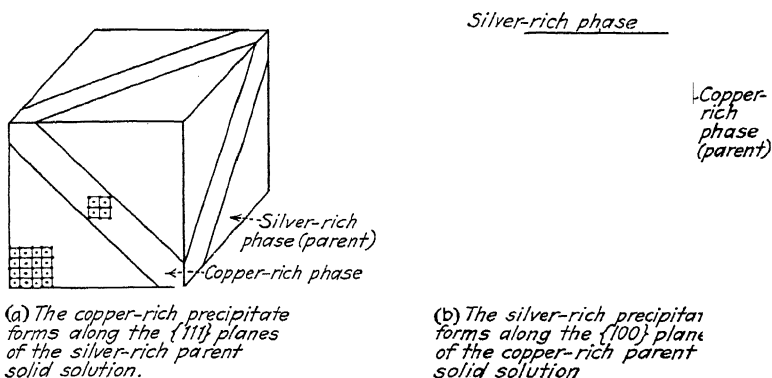
Fig. 81.—The mechanism of precipitation of a derived phase in the copper-silver series. (*After Barrett, Kaiser, and Mehl.*)
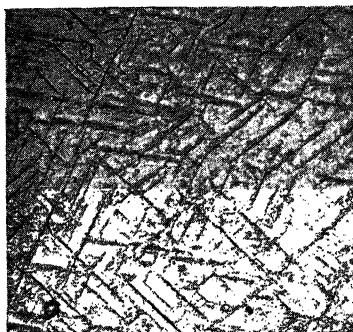
Fig. 82.—Widmanstätten structure in a 50 atomic per cent gold-copper alloy. 500×. (*Photograph by Peterson.*)

Fig. 83.—Widmanstätten structure in copper-tin alloy (59 per cent copper). 500×.

structures shown in Figs. 82 to 92. In Fig. 81a is shown a diagram illustrating the separation of a face-centered cubic phase along the {111} plane of a similarly structured parent phase. This manner of segregation of a derived phase is not an invariable
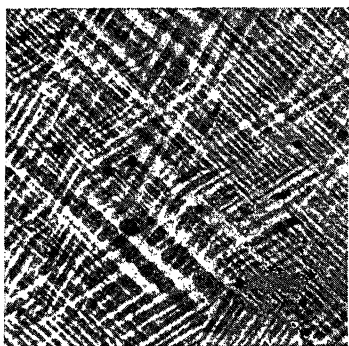
Fig. 84.—Widmanstätten structure in gold-copper-zinc alloy. 100×. (*Photograph by Peterson.*)
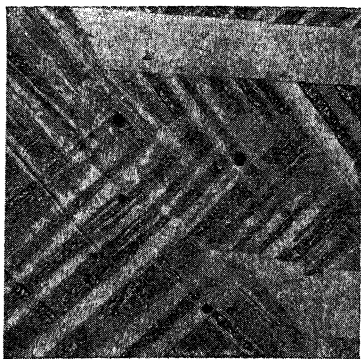
Fig. 85.—Widmanstätten structure in gold-copper-zinc alloy. 100×. (*Photograph by Peterson.*)
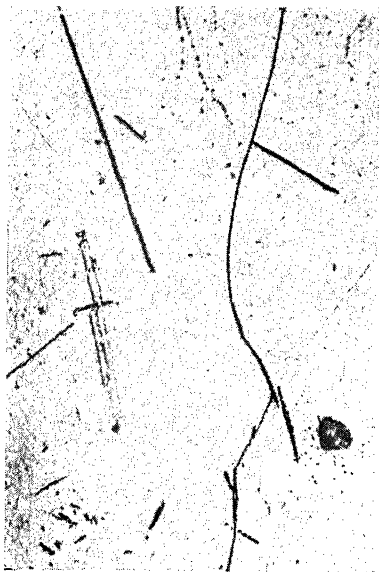
Fig. 86.—Widmanstätten structure in an iron-nitrogen alloy. The "needles" (really, plates) of iron nitride have precipitated along the crystallographic planes of the ferrite. 500×. (*Photograph by Reed.*)
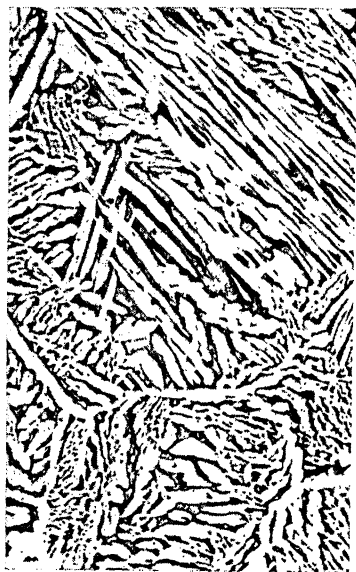
Fig. 87.—Widmanstätten structure in a copper-zinc alloy (brass). 40 per cent zinc. 100×.
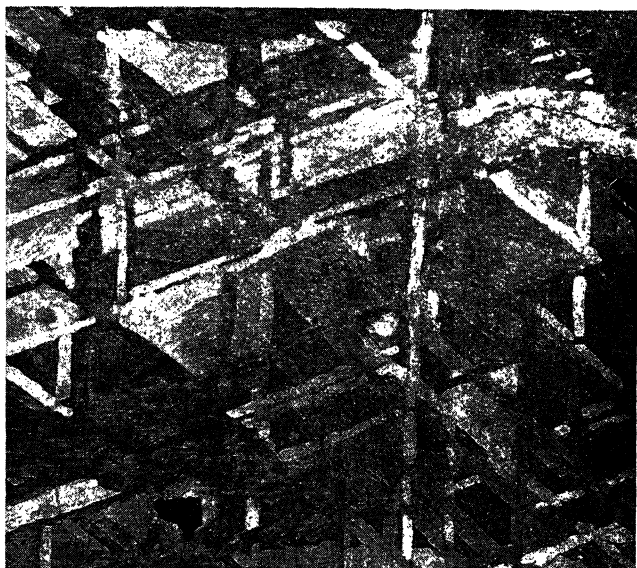
Fig. 88.—Widmanstätten structure in the Casas Grandes (Chihuahua, Mexico) meteorite. 7.74 per cent nickel. One iron-nickel phase (solid solution) has separated from another along cleavage planes. 1⅛ X. The meteorite is the property of the Peabody Museum, Harvard University. (*Photograph by Chow.*)
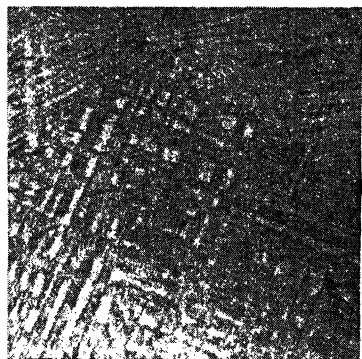
Fig. 89.—Widmanstätten structure in gold-copper-zinc alloy. 500 X. (*Photograph by Peterson.*)

Fig. 90.—Widmanstätten structure in a 30 per cent manganese iron-manganese alloy. 100 X. (*Photograph by Chow.*)

occurrence for other planes than the octahedral planes may, at times, be involved.   In (*b*) of Fig. 81, we have an illustration of an alternative method of separation which Mehl and his associates found to hold for the copper-rich copper-silver alloys. Here the silver-rich solid solution precipitates along planes parallel to the {100} planes, the cubic planes of the parent.

Fig. 91a.—Widmanstätten structure in a cast 0.53 per cent carbon steel.   The ferrite (white) has precipitated mainly along the octahedral {111} planes. 100 ×.   (*Photograph by Chow.*)

Typical Widmanstätten patterns found in a variety of alloys are given in Figs. 82 to 92.   It is suggested that careful attention be given them.

When a high-carbon (say, 0.90 per cent) steel is heated to above where the gamma modification of iron becomes the stable phase (above the point *s*, Fig. 38), the carbon is wholly interstitially distributed (dissolved) within the gamma iron lattice. In conformity with the custom of naming the metallographic constituents of the iron-carbon series, this solid solution of carbon in gamma iron is called austenite.[1]   When this solid

[1] Named after Sir Roberts-Austen, the English metallurgist.

solution, or austenite, is slowly cooled through the temperature (point *s*) where the $\gamma \rightarrow \alpha$ transformation occurs, the solid solution changes, as we know, into an aggregate, pearlite. If, however, the cooling through the transformation is rapid, as may be brought about by plunging the steel into water, a duplex structure, not pearlite, forms. This complex bears the name of

martensite[1] and is the micro-constituent that forms when-ever austenite transforms at such speed that the change occurs at around 200°C., rather than at the normal temperature of 700°C., or thereabouts, for a steel of this composition. The probable nature of martensite is considered elsewhere. We are interested now in the sim-pler matter of its micro-appearance. This is shown in the photomicrograph of Figs. 93 and 176*b*. Obviously, we are dealing with a Widman-stätten pattern. This obser-vation is more convincing in the photomicrograph of a dras-tically quenched carbon-free iron given in Fig. 92. Mani-festly, the decided Widman-stätten pattern in the alpha

Fig. 91*b*.—Widmanstätten structure in a cast 0.53 per cent carbon steel. Precipitation of the ferrite has occurred mainly along the cubic planes. 100×. (*Photograph by Chow.*)

iron delineates the octahedral planes of the old gamma crystallites. Here, the rearrangement of the atoms from the densely packed {111} planes of the face-centered cubic gamma iron to the densely packed {110} planes of the body-centered alpha iron is a small matter involving a change of position of a few per cent only.

c. Inter- and Intracrystalline Segregates.—Inclusions within and without the grain, differ widely with respect to genesis and nature, and as to shape and size. Many inclusions are non-metallic—oxides, sulphides, silicates, etc.—and are residual

[1] Named after the eminent German metallurgist, Martens.

Fig. 91c.—Widmanstätten structure in a cast 1.36 per cent steel.   Some precipitation of the cementite, or iron carbide Fe_3C (white) has taken place along the grain boundaries, but most of the precipitation has occurred along the cleavage planes within the body of the grains.   100 ✕.   (*Photograph by Chow.*)

Fig. 92.—Widmanstätten structure (in relief) in electrolytic iron that has been rapidly quenched in mercury from above 900°C.   The change in volume incident to the gamma⇌alpha phase change at 904°C. has produced the relief effect. 100✕.   (*Photograph by Chow.*)

portions of reaction products which have become mechanically entrapped in the solidifying metal. Examples of such non-metallic inclusions (sonims) are shown in Figs. 96 and 97. They

Fig. 93.—Martensitic structure in quenched iron-carbon alloy (1.16 per cent C). Dark = martensite; white = partly austenite. 500×. (*Photograph by Reed.*)
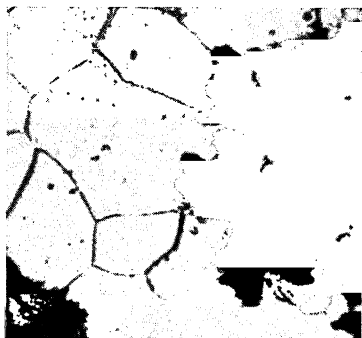
Fig. 94.—Malleable cast iron. Graphite (black) in ferritic matrix. 500×. (*Photograph by Reed.*)

are commonly irregular to rounded in shape if occurring within the grain (Fig. 97), but may conform to the shape of the boundary if present in the intergranular spaces (Figs. 98 and 100). Some

Fig. 95.—Gray cast iron. Graphite inclusions in ferrite. 500×. (*Photograph by Reed.*)
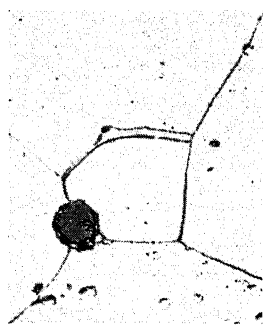
Fig. 96.—Iron oxide inclusions in commercially pure iron. 500×. (*Photograph by Reed.*)

of these inclusions are plastic, notably the high ferrous-oxide silicates. The slag inclusions in wrought iron are of this class (Fig. 99). This ferrous alloy is hot-rolled at a temperature where

the iron is in the gamma condition.   Both the gamma crystallites
and the slag enclosures are deformed (elongated).   On cooling
back to room temperatures, the gamma grains transform into
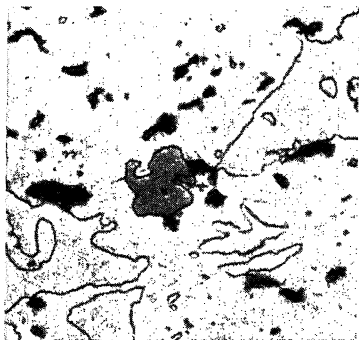
FIG.   97.—Manganese   sulphide
(gray) in cast iron.   (*Photograph by
Anthony.*)

FIG. 98.—Iron sulphide inclusion
in   iron.   500×.   (*Photograph   by
Reed.*)

equi-axed alpha grains while the nonpolymorphic slag inclusions
remain permanently elongated.

Included material may also result from phase and other
changes taking place within the solid alloy.   The separation
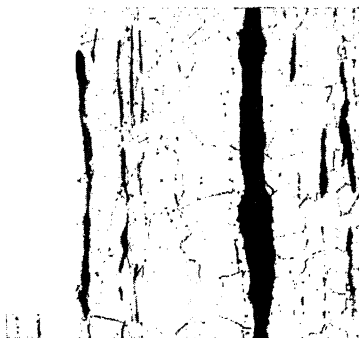
FIG. 99.—Slag (an iron silicate)
inclusions in wrought iron.   100×.
(*Photograph by Reed.*)
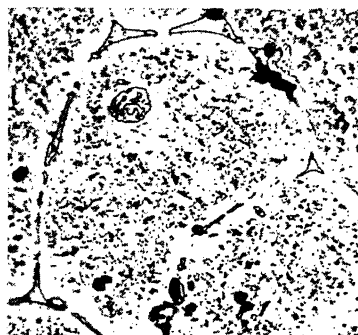
FIG. 100.—Copper aluminide in-
clusions   in   an   aluminum-copper
alloy.   100×.

of graphitic carbon in gray cast iron (Fig. 95), and the formation
of temper carbon during malleabilization of white cast iron
(Fig. 94) are two examples; the precipitation of a solute from a

supersaturated solid solution on very slow cooling is another (Fig. 100).

The effects of inclusions on the physical properties of the metals and alloys vary, naturally, with their number, with their nature, and with their manner of distribution. Obviously, if present in sufficient amounts to reduce materially the effective sectional area, inclusions will impair the strength properties. The effect on the fatigue and impact strength properties may be occasioned by the inclusions acting as foci for localization of stresses. The corrosion resistance of "dirty" metals and alloys
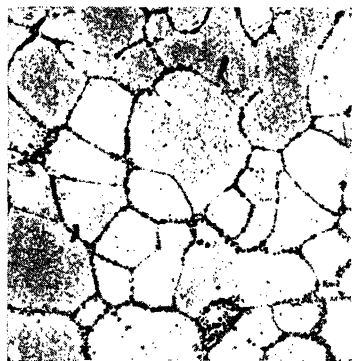
FIG. 101.—Lead inclusions in copper. 100×.
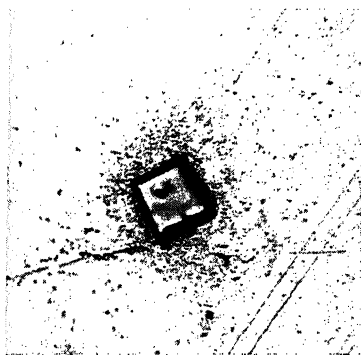
FIG. 102.—Titanium nitride inclusion in steel. Unetched. 500×. (*Photograph by Reed.*)

is commonly inferior to that of "clean" materials. Dissimilarities in chemical constitution, even if quite localized, may instigate galvanic action. Grain boundary enclosures (see Fig. 98), especially if brittle or fusible, lower formability through creating a want of normal coherence between the several crystallites, thus destroying the ductility of the whole, though, in no way, affecting the ductility of the constituent parts. Through this same lack of coherence, the machinability of the alloy may be increased. Lead inclusions in copper and in its alloys (lead is insoluble in copper and in its alpha and beta solutions), graphite in cast iron and iron sulphide in mild steels improve the machining properties of these materials.

CHAPTER VI

THE PROPERTIES OF ALLOYS

Some typical metallic properties, of immediate interest because of their definitive value, were named and discussed in Chaps. I and II; that discussion was confined, under the circumstances, to certain selected properties as related principally to the pure metals. But the properties which we commonly associate with the metallic elements, and especially those of greatest serviceability, attain their full stature only in the alloyed metals, so the more comprehensive survey of metallic properties made desirable by reason of their technical importance has been delayed till such time as some knowledge was had of alloy constitution.

For convenience in study of so numerous and varied an assortment, we may classify the properties of alloys into three main, if not always wholly unrelated, groups:

    I. Mechanical properties.
    II. Chemical (physicochemical) properties.
    III. Physical properties.

We shall now consider properties in some detail, but always with the thought of the relationship to alloy constitution in mind. We shall begin with a discussion of the mechanical properties.

I. Mechanical Properties.[1]

    1. Strength properties (in tension, torsion, etc.).
        a. Ultimate strength, the elastic limit, the proportional limit, the yield point.
        b. Toughness (impact strength).
        c. Hardness.
    2. Plastic properties (ductility).
        a. Elongation and reduction in area.
        b. Bend test.
        c. Cold formability.

[1] The author is indebted to Dr. John Johnston, Director of Research, The United States Steel Corporation for the main part of this outline. Published in the *United States Steel Quarterly*, Autumn Number, 1930.

3. Endurance properties (fatigue).
   a. Repeated bending, impact, tension, etc., tests.
   b. Creep yielding.
4. Wear (abrasion) resistance.
5. Machinability.

The strength properties may be variously evaluated, but we are not especially concerned here with property-measurement methods. Our interest is rather in what the methods tell us about property changes with respect to alloy constitution. In the correlation of strength properties with alloy structure, we shall limit ourselves to those properties determined by the tensile and hardness tests, the two perhaps most generally useful
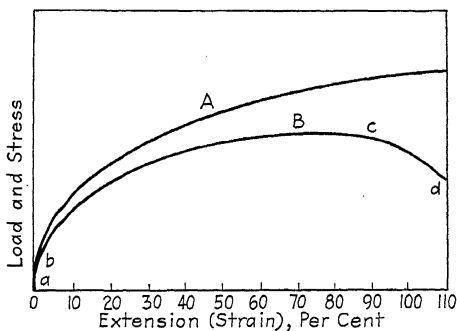
FIG. 103.—Stress-strain diagrams. *A*, stress-extension curve; *B*, load-extension curve.

methods of mechanical property valuation. In the tensile test, the progress of testing, *i.e.*, the progress of the deformation (extension) of the specimen with increasing load, can be most readily followed by referring to a typical stress-strain curve, such as the one given in Fig. 103.

When a tensile stress of low value is applied to a tensile specimen, there results an elastic deformation, a strain that persists only during actual application of the load. With the removal of the deforming load, the specimen returns to its original size and shape. But on continued loading with ever increasing higher stresses, there comes eventually a time when the above no longer is true and a return to original dimensions does not follow on release of the load. The metal has then been stressed beyond its *elastic limit*. It takes on what is called

a "permanent set." Up to the elastic limit and somewhat beyond, extension or strain is proportional to the stress (Hooke's law). This particular portion of the stress-strain curve, wherein strict proportionality exists, is given by the part *a-b* of Fig. 103. (The elastic limit, *per se*, does not show on the curve.) With still further loading, values of stress are soon obtained where proportionality between stress and strain does not prevail. From this point on, a given increment of stress does not result in an equal amount of strain (extension), but in an increasingly larger amount up to the maximum stress. However, as the load is further increased slightly above the proportional limit, point *b*, the metal begins to deform more rapidly. Indeed sometimes as in the case of certain ferrous alloys, the yielding of the metal
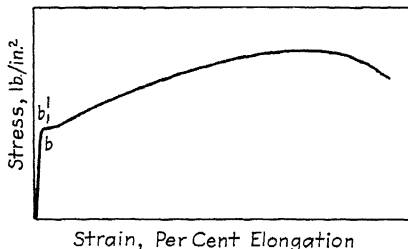
Fig. 104.—Stress-strain diagram of a mild steel (or a commercially pure iron), showing a definite yield point, b_1'.

may occur actually faster than the load can be applied, and the result is then no change, or even a drop, in the load.   (See, for example, point b_1' of Fig. 104.)   This is the *yield point* in these alloys.   In the general case, however, such definiteness in yielding is absent.   The yield point is then taken at some arbitrary value, *e.g.*, the load required to produce a permanent extension of 0.2 per cent.

If the load from yield point to rupture is plotted against the original cross section, one gets the conventional stress–strain diagram (curve *B* of Fig. 103), but the better way of plotting the two values, since it tells the story of the stress-strain relationships more faithfully, is the one which results in the stress-extension curve *A* of that figure.   This curve is obtained by plotting load against the actual area supporting the load.   Point *c* in curve *B* is the maximum load; passing it, rapid extension

of the specimen takes place, but it is now localized. There results a constriction or "necking down" of the specimen at some place along its length. This, in turn, results in a final (breaking) load *d* that is somewhat below the maximum. Fracture occurs in the "necked" portion of the specimen.
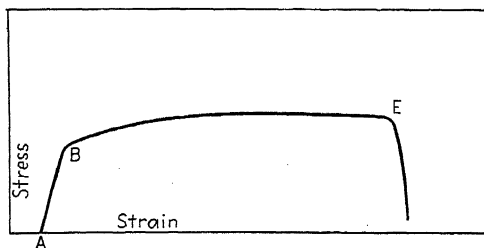
FIG. 105.—Stress-strain curve (in torsion) of wrought iron.

Values for strength properties are not the only data to be obtained from the tensile test; information concerning certain plastic properties is supplied also. The difference in the sectional area of the original bar and that of the broken one at the point of fracture, expressed as percentage *reduction in area*, is one measure of the ductility (plasticity) of the metal. Another is the increase in length, again expressed in percentage *elongation* of the bar during the test.
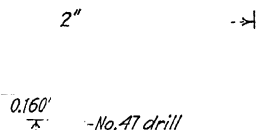
FIG. 106.—Charpy impact specimen.

The stress-strain curve of the torsional test is given in Fig. 105.

The tensile test serves admirably as a means of static testing the properties of a metal. But, on occasion, the properties should be evaluated preferably by a suitable dynamic test, in order to simulate, as far as is possible in a laboratory test, the actual conditions the metal may encounter in service. There it may be called upon to resist stresses that are not always slowly

applied. Dynamic testing methods give one an idea of the shock resistance of a metal, or, as it is usually called, its *impact strength*, which essentially is a measure of the toughness.

One simple way to do this is to measure the height of rebound of a falling weight, the principle which is the basis of the Shore scleroscope "hardness" tester. A more widely used method, however, is the Charpy or Izod impact test, where a weighted pendulum is dropped from a known height to strike a securely fixed, accurately notched specimen (see Fig. 106). The arc traced by the pendulum subsequent to fracturing the specimen indicates what portion of the kinetic energy of the falling pendulum was absorbed in the work in fracturing the bar. The tougher the metal, the greater the amount of the energy absorbed and the shorter the postnadir path of the pendulum; or perhaps, to state it more accurately, the tougher the metal, the greater the rate of energy absorption (conduction and dissipation internally away from the point of impact), and the shorter the path. The *impact strength*, or *notch toughness*, is then expressed as the energy, in foot-pounds, absorbed in rupture divided by the original sectional area of the specimen.

That particular manifestation of strength which we call hardness is not readily defined, yet a certain *kind* of hardness, *i.e.*, indentation hardness, is the one property which is perhaps most easily evaluated. This particular method of hardness measurement is to force an extremely hard penetrator, by the use of a standard load, into the smoothed surface of the specimen. The magnitude of the indentation produced, as indicated either by the diameter, by the depth, or by the superficial area of the depression relative to the load, becomes a measure of the resistance to penetration, that is to say, of the penetration hardness of the material. Obviously, plastic flow is involved in the test, and the measurement of the penetration hardness of nonductile materials—as, for example, most intermetallic compounds, or even of the brittle simple metals, as antimony—if possible at all, produces results either quite meaningless or of questionable accuracy.

The measurement of the rebound or elastic hardness of metals by the Shore scleroscope has been mentioned above, and another kind of hardness, mineralogical or scratch hardness, will be referred to later in this section.

Like the file test for hardness, the bend test for ductile metals (wire and strip) is easily made, and the results obtained are readily comprehended by anyone. In this test, one finds the number of bends back and forth through a certain angle, commonly 90 deg., a metal wire can experience before rupture occurs. In a rather convincing way, the bend test also gives one an idea of strain-embrittling susceptibility since the bending, to and fro, progressively deforms the metal, strain-hardening it locally.

A bend test of another sort is occasionally used for brittle materials. Here the test specimen, a circular or square section bar, is loaded as a simple beam. The "tensile strength in bend" may be calculated from the formula

$$S = \frac{PlW}{4(2\theta)},$$

where S = bend strength, P = the load, l = the length of the specimen, and W = the thickness of the specimen. θ is the moment of inertia of the section.

Sheet metal is commonly fabricated by deep drawing to shape. This operation requires a high degree of toughness (tenacity combined with plasticity) in the material worked. The formability of sheet, or its deep drawing quality, may be determined by the Erichsen test. In this test, a piece of sheet is slowly forced by a rounded mandrel through a cup-shaped die. The depth of the perfect, *i.e.*, nontorn, cup produced is indicative of the suitability of material for deep drawing work.

In the tensile and other similarly acting strength-evaluating tests, the application of the deforming stresses is continual and sustained until rupture; moreover, it is in one direction only. But stresses are encountered in service, notably by the moving parts of machines which are not characterized by continuity of application or by constancy in direction, and a metal's properties, as determined by one or more of the tests already mentioned, may be no criterion of its so-called *endurance* or *fatigue* properties. The "endurance limit" is the aspect of fatigue that is of interest. One common way—the so-called rotating-beam test—is to rotate a standard specimen loaded as a simple beam, with successively increasing loads, and note the number of revolutions required to rupture the specimens. During the application of the stress, the uppermost fibers of the slightly flexed specimen are, at any

instant, in compression, the ones opposite are in tension. A half revolution of the specimen alternates these conditions; so with each cycle every peripheral crystallite is stressed alternately by forces that act in opposite directions. If the repeated alternating stress is low, the number of cycles may be indefinite, or exceed a safe finite value of, say, 10,000,000 or more. As the applied load becomes larger, the number of cycles to fracture becomes smaller and smaller. The highest maximum stress consistent with long life is the endurance limit. A diagram showing the relation between cyclic number and stress is shown in Fig. 107.
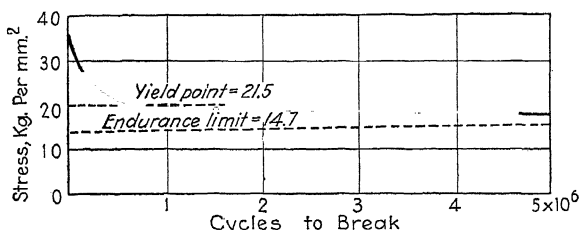
Fig. 107.—Fatigue diagram of an 0.08 per cent carbon steel (tensile strength = 36 kg. per square millimeter). (*Schwarz.*)

When metals are stressed for long periods of time, particularly at elevated temperatures, even with loads well under the elastic limit, it may be found that the metals slowly and perceptibly yield. This manner of long-time yielding is known as *creep*, and the amount of creep yielding for a given metal is a function of the temperature, of the load, and of the time of application of load.

Scratch hardness is, perhaps, the earliest attempt to rationalize the widely variant hardness of different materials. It is the basis of the Moh scale of comparative hardness of minerals. Scratch-hardness testing methods are useful in making micro-hardness measurements on alloys; *i.e.*, in the determination of the relative hardness of different constituents of a conglomerate alloy. This may be done either by comparing the widths of the scratches made by passing the polished specimen beneath a weighted stylus, or by comparing the loads necessary to produce scratches of equal width. Scratch hardness is evidently related to wear-resistance properties. As a matter of fact, the more

usually determined indentation hardness, by the Brinell, Rockwell, or Vickers method (see Fig. 109 for equivalent values) is
equally indicative of the quality of this property. This is shown, for four iron alloys, in Fig. 108.

In bearing alloys (antifriction metals), the question of wear resistance is, of course, important, since among other things it determines the life of the bearing, but toughness and compressile strength are also involved. The bearing must not shatter under forces suddenly applied, and it must not

on vario
145 Vicke
hardness; *B*, 2.20 per cent Ni, 12 per cent Cr, 204 Vickers hardness; *C*, 0.10 per cent Ni, 12 per cent Cr, 258 Vickers hardness; *D*, nitrided steel. (*Hengstenberg.*)

flow out under the load. Hard metallic substances, notably the intermetallic compounds, are ideal as antifriction materials from the points of view of wear resistance and strength, but for
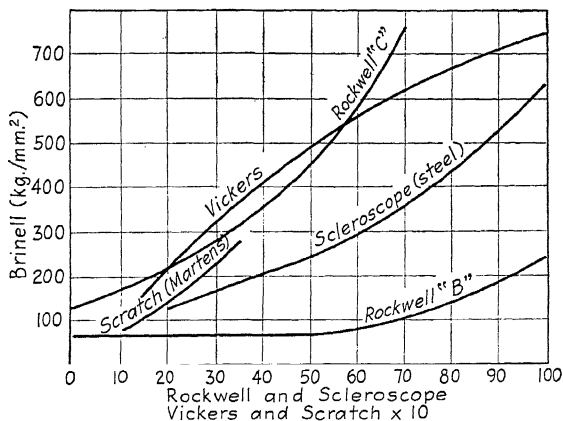
G. 109.—Approximate Brinell hardness equivalents. (*After Schwarz.*)

use alone and unsupported they are ruled out because of their lack of any appreciable degree of toughness. Commercial bearing alloys, such as Babbitt metal (see Fig. 64), are commonly conglomerates, made up (*a*) of a tough, strong

matrix that will support and conform to the shape of the shaft, and (*b*) discrete particles, of microscopical dimensions, of hard, intermetallic compounds disseminated uniformly throughout the softer, tougher ground-mass. These hard enclosures bear the actual load.

The last-listed property of the mechanical group, *machinability*, deserves comment not only because of its economic importance in metal fabrication and finishing, but also because metallographic constitution plays some part in determining this property. Metal objects and parts are frequently turned, milled, or planed to size and shape, and they may be drilled, tapped, or otherwise machined. The property of machinability in metals and alloys is a complex one, subject to many variables, and involving in some measure simple properties of both the strength and plastic groups. Values for a particular simple property, as hardness, do not ordinarily constitute a reliable index of machinability, though it is true that extremely hard materials do not machine well, nor do those which are very soft, or tough. Again, the ease of machinability differs widely with the particular machining operation; a metal that may be easily turned, for example, may not so readily be drilled. Extremely hard substances machine with difficulty (and with rapid deterioration of the cutting edge) obviously because of the small difference in the hardness of the tool and of the material. Soft, plastic metals, like lead, saw, drill, etc., machine badly, not because of the softness *per se*, but because such materials are commonly tough, preventing the formation of a clean-cut chip, *i.e.*, one that frees itself readily from the material undergoing machining. It would seem, generally speaking, that good machinability requires a hardness in the subject that is not too high, nor, on the other hand, so low that the material possesses excessive plasticity and toughness.

Machinability is most reliably evaluated by an actual service test, where either the quantity of chips produced in a given time or the energy required to give a certain weight of turnings may be used as the measure of the machining quality.

The machinability of a metal or alloy is influenced by the microstructure, by the physical condition, and by the chemical composition. The microstructure largely determines the strength and plastic properties, but it also is of moment in determining the character of the chip. A small grain size (in

certain brasses) definitely improves the machining properties. In duplex alloys, one constituent may favor machinability more than the other, an example of which is found in the alpha and beta brasses where the machinability improves as the beta phase decreases. In the high-carbon, iron-carbon alloys (the cast irons), machinability differs with the structural conditions possible in the alloys. These alloys may be classified according to their microstructure, and in order of their machinability, as follows:

1. Ferritic (free carbon and ferrite); see Fig. 95.
2. Pearlite-ferritic (free carbon, ferrite and pearlite).
3. Pearlitic (free carbon and pearlite).
4. "Mottled" iron (pearlite, free carbon and some massive cementite).
5. White iron (pearlite and massive cementite).

In the alloys of lower carbon content—the eutectoid and hypereutectoid steels—microstructure is again of some influence on machinability. If the cementite of such steels is in the form of small spheroids—a condition that may be brought about by heat-treatment—the steels are decidedly more machinable than if the cementite is in the usual pearlitic (laminated) condition. In spheroidized steels, the cutting tool pushes the small, hard spheroids aside as it encounters them, while in pearlitic steels the tool must cut through the cementite plates.

Alloys of iron (and of iron and carbon), containing alloying elements, as nickel, manganese, etc., in amounts sufficient to preserve the gamma phase at room temperatures, give difficulty in machining owing to the cutting action locally deforming the metastable solid solution (austenite) which results in the transformation, *in situ*, of a small amount of the austenite to a hard, essentially ferritic martensite.

It has been inferred above that the character of the chip has some bearing on machining qualities. In addition to inherent plasticity as affecting this factor, the presence of enclosures in the metal or alloy may be of some effect. These inclusions, because they break up the continuity of the matrix, change a long, torn turning into small, clean chips. Iron sulphide inclusions in mild steel, and lead in copper and brass, are examples of enclosures whose effect on machinability is definitely favorable. Lead is insoluble in copper and in its alpha and beta solutions

(see Fig. 101). The insoluble lead consequently segregates, forming small, rounded inclusions. Their presence in the turning lowers its tenacity and renders it distinctly "tender." It breaks into small chips as fast as it forms, thus clearing immediately the path for the entering tool. In Table 10, are given some comparative values of machining properties (and strength and hardness, also of some interest) of copper and some of its alloys, with particular reference to the effect of lead.

TABLE 10.—THE RELATIVE MACHINABILITY OF COPPER AND CERTAIN OF ITS ALLOYS WITH LEAD AND ZINC
(After A.M.S. Handbook)

Composition, per cent			Tensile strength	Hardness Rockwell B	Relative machinability,* per cent
Cu	Zn	Pb			
100.0	..	...	35,000	23	20
98.5	..	1.5	25,000	23	80
60	40	...	50,000	67	35
60	38	2.0	50,000	67	80
62	35	3.0	45,000	57	100*
62	34	4.0	45,000	57	110

* Free-cutting rod (drill temper) = 100 per cent.

Properties versus Composition (Constitution).—In the foregoing discussion little mention has been made of the effect of alloy composition, that is to say, of constitution, on property variation. We did see, in the case of machinability, that the presence of a properly disseminated insoluble constituent, as lead in copper or brass, was effective as regards the changing of this particular property. The efficaciousness of the lead inclusions in these materials is a consequence of lead's insolubility. Their action is purely a mechanical one. But, had the lead been soluble—wholly or in part—what then? Let us be more general, and let us consider a simpler property than machinability; moreover, let us take one the number of whose individual determinations under every structural condition possible in alloys warrants us to draw general conclusions therefrom. Strength is one such property; hardness is another. How, for example, is the hardness of one metal modified by alloying with it another

metal of a different hardness when, let us say, the two form a simple, eutectiferous series? Or, to put the matter more comprehensively, what happens to hardness when two metals alloy in any of the eight possible procedures listed and described in Chap. III?

The answer to these questions, in any particular instance, is determined basically by the alloy constitution, *i.e.*, by the nature, the number, and the distribution of the primary constituents present in the alloy. In Fig. 110 is given a group of ideal hardness-composition curves for a number of the type alloy systems of Chap. III. For convenience, each hardness curve is shown with the corresponding equilibrium diagram. In (*a*) is given the hardness-composition curve of the Group II*a* series of alloys, a series which shows complete solid insolubility. The ideal hardness curve of this series is a straight line connecting the hardness of one metal with that of the other. We have seen in our study of the properties of solid solutions that this particular alloy constituent is uniformly harder than at least one metal, and that the maximum hardness of an isomorphous solid-solution series occurs in those alloys approximating equiweight composition. The ideal hardness curve of such a series (Group I alloys) is given in (*c*). In a series (*b* of Fig. 110), where partial solid solubility exists (Group II*b*), there is, as one would expect, an increase in hardness over that of the pure metals within the solid solubility range at either end of the series (h_a-*c* and *d*-h_b of Fig. 110*b*), whereas the hardness varies lineally within the two-phase field. Had solid solubility been complete, the hardness curve might have followed the dotted line *c-f-d*, which is simply the continuation of the curves h_a-*c* and *d*-h_b.

Intermetallic compounds are normally hard constituents, and their presence increases the hardness of the alloy. In (*d*) of Fig. 110 is shown the hardness curve of a compound-containing series (Group II*c*). There is a maximum in the curve at composition of the compound. To the right or left of the compound, the curve is a straight line, as one would expect of any eutectiferous series. In the curve as given, the hardness of the compound is higher than that of either metal. This is not invariably so. The compound's hardness may, for example, lie between the hardnesses of the two metals. Then there is an inflection and not a maximum at point *c*. In Fig. 110*e* is given

the hardness curve of a eutectiferous series with a compound of the "hidden-maximum" type, and one terminal solid solution.
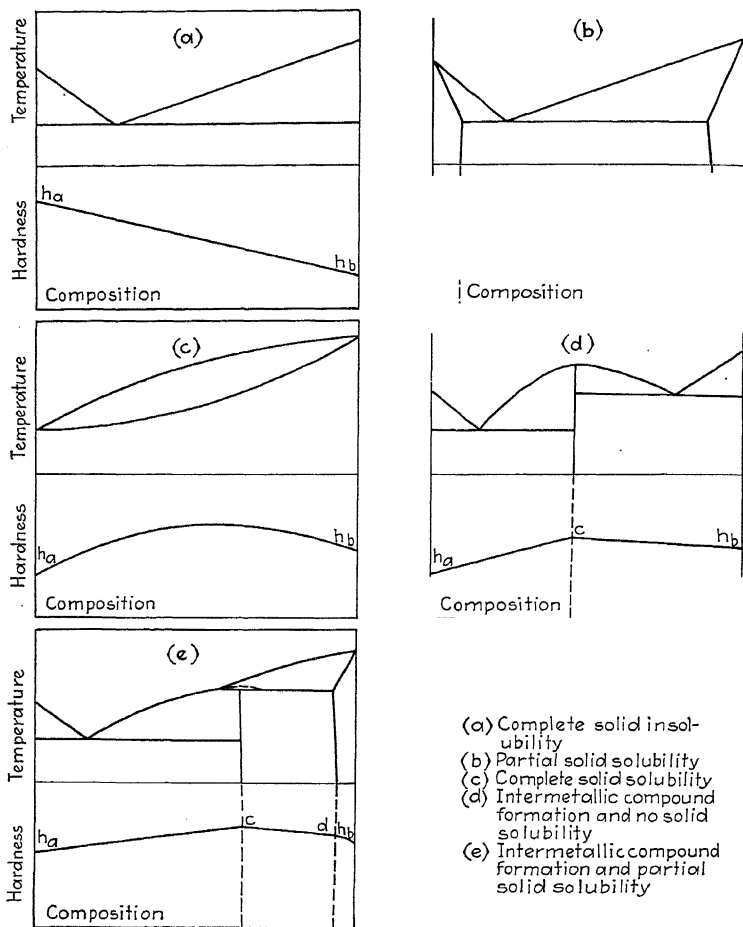
FIG. 110.—Hardness curves in relation to constitution.

(a) Complete solid insol-
ubility
(b) Partial solid solubility
(c) Complete solid solubility
(d) Intermetallic compound
formation and no solid
solubility
(e) Intermetallic compound
formation and partial
solid solubility

These two structural features of the series are reflected in the shape of its hardness curve.   No comment seems necessary.

Experimentally determined curves (hardness, strength, etc.) of actual alloy systems may depart from the ideal curves, as

shown. This is because factors other than alloy constitution, such as grain size, degree of dispersion, etc., commonly enter into the determination of hardness. The hardness-composition curve of an actual isomorphous series (copper-nickel) has already been given in Fig. 46. The hardness and strength (vs. composition) curves of the aluminum-rich aluminum silicon are shown
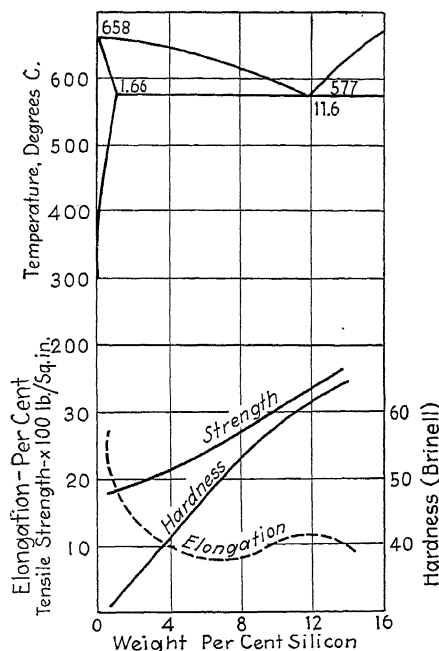
FIG. 111.—Strength-property *vs.* composition in the aluminum-rich aluminum-silicon alloys.

in Fig. 111; this series approximates, as closely as any perhaps, the rare condition of complete insolubility at ordinary temperatures. The strength-property curves of more complex binary series are shown in Fig. 112 (the magnesium-silver series), and in Fig. 113 (the copper-zinc series).

The want of exact coincidence of changes in direction in the property curves and the appearance of a new phase, as noted particularly in the latter two series, is in part due to the circumstance that a new phase is ordinarily not detectable by mechanical

testing methods until appreciable amounts are present.   Also, the question of equilibrium enters here.   Since the equilibrium diagram depicts alloy constitution under equilibrium conditions, it is quite necessary, if parallelism between property and constitution is to be approximated, that the alloys be tested only after an adequate homogeneization treatment.
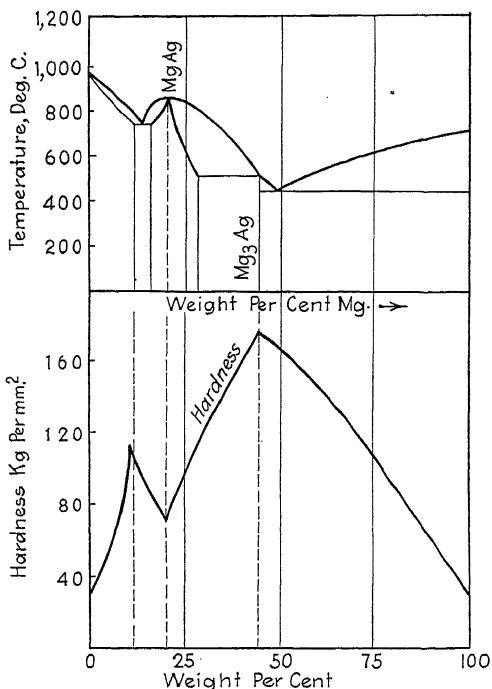
FIG. 112.—The hardness of magnesium-silver alloys as dependent on constitution.

Properties   versus   Temperature,   Etc.—A   polycrystalline alloy's strength properties are, in part, inherently atomic, but some portion is genetically structural, *i.e.*, this latter part is the consequence of the particular structural and granular character of the crystalline aggregate.   While temperature, for example, influences strength properties quite independent of their genesis, other factors influence strength essentially through alteration of the gross structure.   For instance, in certain types of critically

dispersed conglomerates, the dispersion, *i.e.*, the particle size, of the discontinuous phase may become the controlling factor. The hardness of such so-called age-hardenable alloys is mainly determined by the heat-treatment procedure followed (see page 237, Chap. VII).

Any particular mechanical property of the metals is thus not independent of the prevailing external conditions, temperature principally, or of the granular character of the conglomerate.
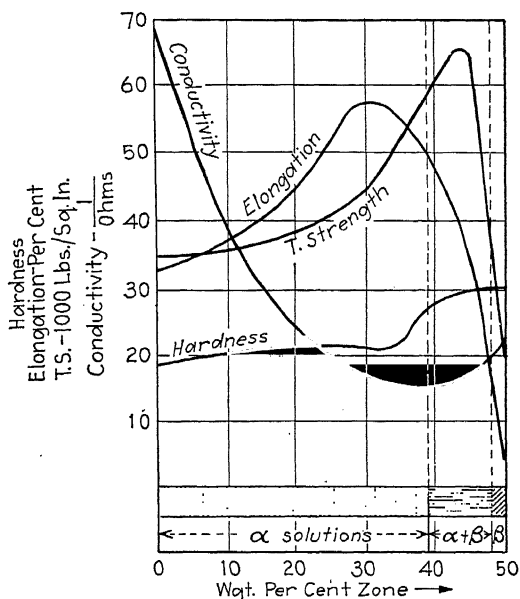
FIG. 113.—The properties of the high copper brasses.

It is this latter circumstance that makes possible the alteration of properties by suitable heat-treatment. While the fact of the greater technical importance of alloys than of the pure metals may in part rest on the range in properties that may be secured by changes in chemical composition in the former materials, it is also due to the circumstance that alloys, because of their comparatively greater structural complexity, admit of larger possibilities in property change through manipulation of external controlling factors. In other words, alloys owe a large part of

their superior technical importance to their greater susceptibility to property variation by simple heat-treatment. The importance of this phase of metallographic science warrants treatment in a separate chapter (Chap. VII). We shall, however, cite a few
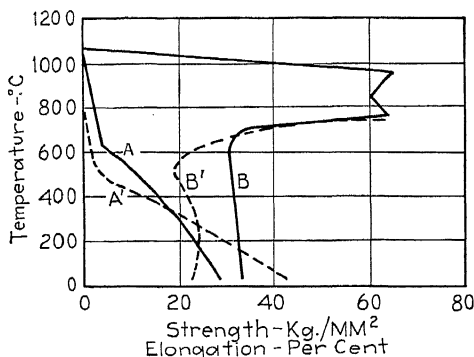
FIG. 114.—Influence of temperature on the strength and ductility of copper and a 60 per cent copper brass. *A*, strength of copper; *A'*, strength of brass; *B*, ductility of copper; *B'*, ductility of brass. (*After Bengough.*)

typical examples of property's dependence on environment or on the physical condition of the alloy.

1. *Temperature.*—The effect of temperature on the mechanical properties of copper and one of its alloys (brass) is shown by the curves in Fig. 114. The general effect is the same in the two cases—a decrease in the strength properties and an increase in the ductility (at least, till near the melting temperatures) with increase in temperature. The effect of sub-zero temperatures on the strength and plasticity of iron is given in Fig. 115.
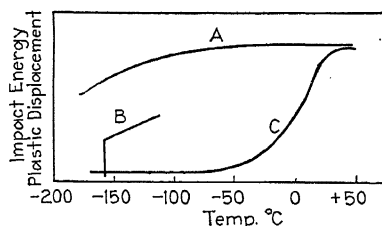
FIG. 115.—Influence of low temperatures on (*A*) angular displacement in torsion, (*B*) elongation in tension, and (*C*) energy absorbed in impact. (*After Heindlhofer.*)

2. *Grain Size.*—An interpretation of the influence of grain size on the mechanical properties of metals is shown in Fig. 117. The curve *c-d* of that figure gives the grain size-property relationships as found in polycrystalline (cast) metal, that is to say, in

such metal where a sufficient number of randomly oriented grains is involved in the test so as to insure an isotropic character to the aggregate. Under these conditions, the strength properties increase with fineness of grain, while the plastic properties decrease generally. Since a polycrystalline metal is isotropic only because of the random distribution of its many anisotropic grains, successive decreases in the number of the latter progressively lessen the mass effect of random orientation on the property as a whole and, at the same time, bring gradually into prominence, as influencing these properties, the anisotropic character of the
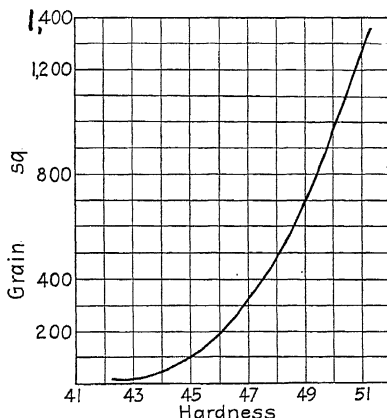
Fig. 116.—Hardness as a function of grain size in brass. (*Elam.*)[1]

constituent units. The limit obviously with respect to reduction in grain count is reached in a specimen containing a single crystal only.

As it becomes a true anisotropic body, the strength and plastic properties of a metal single crystal will vary somewhat with the direction in which they are measured; *i.e.*, these properties are partly vectorial. Assume that points *a* and *b* of Fig. 117 represent the low and high limits, respectively, of these properties in a single crystal of the same metal whose polycrystalline form gives the property-grain size relationships shown by the curve *c-d*. The maximum ductility, point *b*, of the single crystal, *i.e.*, the value of this property as measured in the most propitious direction, is much greater than the best value (point *c*) obtained in testing

[1] From Elam's "Distortion of Metal Crystals," Oxford University Press, by permission of the publishers.

the polycrystalline metal. On the other hand, the maximum strength developed in any direction in a single crystal is lower than the lowest value shown by the polycrystalline aggregate (compare again *b* with *c*). This is in accord with what we know about the strengthening effects of differently oriented grains on one another.

Now let us suppose that we increase the grain count so that instead of having under consideration a specimen consisting of a single crystal, we have one made up successively of 2, 3, 4, . . . , etc. crystals, that is to say, we shall have specimens where grain-size effects play an increasingly important role in the determination of properties. But what, one may ask, is the genetic relationship of curve *a-b*, which represents a condition where anisotropic effects are paramount, to the curve *c-d*
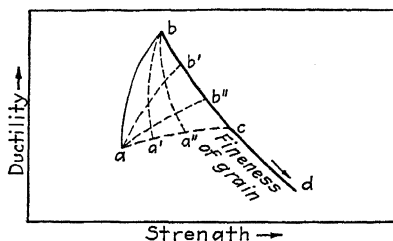
Fig. 117.—Strength properties of metal (cast) as influenced by grain size.
(*After Czochralski.*)

where these are practically negligible? Plainly, the transition from the one to the other is a continuous and gradual one. Conceivably, there are two general effects as regards metal properties, resulting from the substitution of a progressively finer grain metal for one that consisted originally of a single grain: (1) the difference between the minimum and maximum property values, as a peculiar effect of anisotropism, becomes less and less with growing multicrystallinity, *i.e.*, points *a* and *b* approach one another, and (2) both values approach point *c* as a limit. To illustrate (referring to Fig. 117), when a few crystallites make up the aggregate, point *a* moves to position *a'*, and point *b* to *b'*; with further grain refinement (though not to the extent that anisotropic effects shall entirely disappear), point *a* moves still farther along to position *a''*, and likewise point *b* to *b''*. Still further refinement nullifies completely, through sheer force of

crystal numbers, all effects of individual anisotropism. Values *a* and *b* now become equal in magnitude and intersect at point *c*. From that point on, grain size is the main structure factor operative in property determination. The area *a-b-c* represents a condition of quasi-isotropism.

The grain size of brass (63 per cent copper), as related to its mechanical properties, is illustrated in Fig. 116.

3. *Presence of Third Metal.*—The properties of a binary alloy are capable of further modification by the addition of a third, fourth, . . . , etc., alloying metal. The particular effects of the added metal, or metals, depend, as in the first instance, on the precise manner of the alloying mechanism and on the way this disturbs the structural status quo of the parent binary system. Physicochemically, with such cases, we are dealing with a ternary, quaternary, etc., system, whose phasial relationships must be viewed and interpreted in the light of physicochemical principles. But from the point of view of structure and properties, one may regard these multimetal alloys simply as a binary system to which, for particular reasons, special elements have been added. Historically, this has been the way most of our ternary and more complex alloys, as for example the alloy steels, have come into being.

As typical illustrations of the effect of a third metal on properties, we shall cite two instances, where modification is the consequence of two quite different alloying procedures. In the case of the silicon steels—basically, iron-carbon alloys to which silicon is added in small amounts—the silicon influences properties by reason of its solution (substitutionally) in the ferrite. Under these circumstances, the effect is, as one would expect, a generally strengthening one, but because of the inherently brittle nature of the iron-silicon solid solution, the higher strengths are attained at a considerable sacrifice of the toughness. The mechanical properties of some silicon steels are given in Table 11.

Copper and nickel form, as we may recall, a continuous series of solid solutions, for these two metals are mutually soluble in all proportions in the solid state. If, however, one adds silicon to the copper-rich cupronickels, in amounts which approximate the silicide composition, Ni_2Si, the solubility of nickel in copper, in effect, becomes definitely limited, and any nickel in excess of

that solubility is precipitated as the nickel silicide. And, as is characteristic of all solid solutions of limited solubility, the solubility of the nickel, or perhaps one should say, the nickel silicide, in the copper decreases with temperature. This circumstance (and the fact that the precipitate itself is a hard intermetallic compound) furnishes the necessary condition for the phenomenon known as dispersion (or precipitation) hardening. This is a subject that has been referred to previously, and one which will be discussed in some detail, because of its importance, in the next chapter. Our interest in this alloy now, and in others like it, is in the fact that the introduction of a third metal can work profound changes in existing solubility relationships, which fact, under certain other favorable conditions, can be made use of to create property values in the ternary alloy quite unattainable in the simple binary one. We have there (the copper-nickel-silicon alloy) one instance of many where the addition of a third metal makes the resulting alloy more amenable to heat-treatment. This circumstance is what so often makes ternary alloys, notably the alloy or special steels, of especial importance.

TABLE 11.—THE MECHANICAL PROPERTIES OF SOME LOW-CARBON (0.10 – 0.12 PER CENT CARBON) STRUCTURAL SILICON STEELS, AS ROLLED
(*After Paglianti*)

Per cent silicon	Tensile strength, lb./sq. in.	Elongation, per cent in 8 in.	Reduction of area, per cent	Hardness (Brinell)	Impact value
0.37	61,000	29.5	57	131	36.0
0.67	65,000	28.5	58	144	34.2
0.95	69,000	28	55	150	31.5
1.73	80,000	26	40	180	12.0
2.35	83,500	23	39.5	182	10.5

4. *Cold Deformation.*—The strengthening and generally embrittling effects of cold work are shown in the curves of Fig. 118. These effects are technically important for two reasons: First, they may be used to increase moderately the strength and elasticity of metals (particularily of wires), and second, because of the progressive loss of ductility, and thus formability, with increasing amounts of cold work, the amount of deformation that

may be given a metal (or alloy), without meanwhile alleviating the embrittled condition, is severely limited.

Cold deformation has also an indirect effect on properties of wrought and annealed metal, inasmuch as it is one of the factors involved in determining the final grain size of such metal. This matter will claim our attention under the general subject of annealing in the next chapter.

5. *Particle Size.*—In alloys, as for example the copper-nickel-silicon alloy mentioned above, where there is a decrease in the solid solubility with fall in temperature, the excess solute may be made to assume a precipitated form in which it is finely dis-
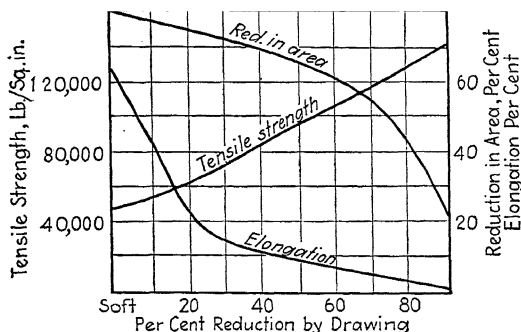
Fig. 118.—Effect of deformation (drawing) on the mechanical properties of a 67 per cent copper brass. (*A.S.M. Handbook.*)

persed throughout the parent solution matrix. If this dispersion be critical, *i.e.*, characterized by a sufficient number of the properly sized particles, an effective resistance to deformation (slip) is developed in the alloy, presumably because the precipitated particles "key" the potential gliding planes. The maximum increase in the strength properties is associated with critical dispersion, and until the discrete particles attain critical dimensions, or, by reason of continued growth, they exceed these —both conditions being a matter of time and temperature— maximum property values do not obtain. A hardness-time (*i.e.*, hardness-particle size) curve of the copper-nickel-silicon alloy mentioned is shown in Fig. 119.

II. Chemical (Physicochemical) Properties.
    a. Corrosion resistance.
    b. Heat resistance.
    c. Diffusion in the solid state.

a. Corrosion Resistance.—As pointed out in an earlier reference, the fact of corrosion susceptibility of the metal should not be surprising.   While structurally, and in certain aspects of behavior, the metals are quite apart from the other elements, they are first and always genuinely elemental, possessors with the nonmetals of a combining urge, and constrained in all points as they are to enter into chemical union.   Corrosion is nothing more or less than a form of chemical (electrochemical) activity.   The rusting of iron is perhaps the best known, and certainly the most dis-
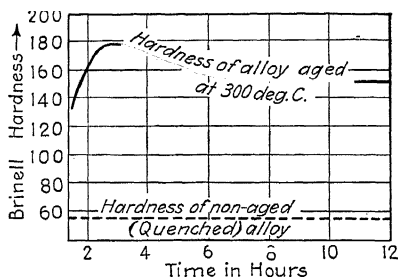
FIG. 119.—Effect of aging time on hardness.   Cu = 97.78 per cent; Ni = 1.77 per cent; Si = 0.04 per cent (Ni₂Si = 2.08 per cent cal.).   (*After Gonser and van Wert.*)

turbing, instance of the corrosion phenomenon.   Let us briefly consider the chemistry of the corrosion process of that metal. It is no simple process, but from the point of view of the electronic theory,[1] it may be outlined in a very simple way.

Iron in air (not necessarily saturated with water vapor) becomes covered with an invisible moisture film.   Because iron is above hydrogen in the electrochemical series, it tends to lose electrons and to dissolve, entering the solution as ferrous ions,

$$\text{Fe solid} + 2\text{H}^+ \rightleftharpoons \text{Fe}^{++} + 2\text{H}^-(\rightleftharpoons \text{H}_2) \tag{1}$$

In water, there is always a certain low concentration of hydrogen and hydroxyl ions,

$$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \tag{2}$$

[1] There is an alternate theory, the acid theory, which postulates, in addition to the oxygen and water of the electrochemical theory, the presence of an acid (carbonic usually).

The amounts of the ferrous ion (Fe^{++}) and of the hydroxyl ion (OH^-) which can exist simultaneously are very small.[1] Consequently ferrous hydroxide will tend to precipitate,

$$Fe^{++} + 2OH^- \rightarrow Fe(OH)_2 \qquad (3)$$
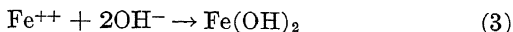
or this will further react with the oxygen to form and precipitate the ferric hydroxide,

$$2Fe(OH)_2 + H_2O + O \rightarrow 2Fe(OH)_3 \qquad (4)$$
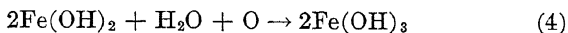
which subsequently may be converted into the corresponding oxide,

$$2Fe(OH)_3 \rightarrow Fe_2O_3 + 3H_2O \qquad (5)$$
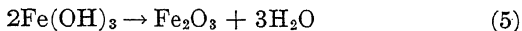
Any condition of chemical or physical heterogeneity (strain) facilitates the corrosive attack, assumably because then different parts of the surface hold electrons with different degrees of tenacity; that is to say, all surface electrons cannot be in equilibrium with the solution at the same time. Those parts of the surface of relatively loose electronic relationships become centers of anodic activity, and other parts act as cathodes. Thus is set up a galvanic cell in miniature, whereby corrosion proceeds in an accelerated fashion.

There are several factors, applicable in general or in specific cases, which influence in one way or another the corrosion process. One, already mentioned, is a lack of chemical homogeneity in the alloy, or even in the commercially pure metal. It seems probable that a piece of an absolutely pure metal, iron, for example, which at the same time is physically uniform throughout, would not corrode. This probability remains definitely unproved, however, since we lack, in the case of iron at least, a metal of that purity. The effect on corrosion of the presence of a second element, even where present in seemingly infinitesimal amounts, depends commonly on the manner of alloying. If a duplex structure in the alloy results from the addition of one metal to another, the corrosion resistance of the alloy will be no better, and may be worse, than that of the more corrodible constituent of the conglomerate. One says that actual impairment

[1] The solubility of $Fe(OH)_2$ at room temperatures is only four parts per million.

may ensue from such an alloying procedure because of the possibility of galvanic action (electrolysis) occurring between the two unlike, discontinuous constituents, making the conglomerate alloy more susceptible to attack than the more corrosible component would be, if it were alone. The observed incipient rusting around inclusions in iron is a case of localized electrolysis, while the preferential attack of certain corrodents on the beta phase of the duplex alpha + beta brasses is an example of selective corrosion.
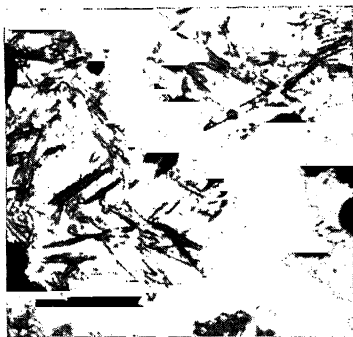
FIG. 120.—Quenched eutectoid steel. White constituent is martensite, black is troostite. The color contrast indicates the much greater susceptibility to the etchant of the troostite than of the martensite. Nital etch.   1000 ×.
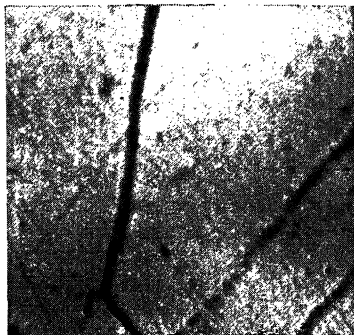
FIG. 121.—Stainless steel (18 per cent Cr and 8 per cent Ni). Chromium carbides precipitated along the grain boundaries.   1650 ×.

In alloys containing a finely dispersed constituent the particle size of the discontinuous phase is of some influence on the corrosion resistance. Where the particle size is small, say of submicroscopic dimensions, the corrosion resistance is commonly much inferior to those alloys where sizable, dispersed particles exist. Troostitic steels (Fig. 120; the constituent troostite represents a condition of coalescence of the cementite just above that found in aged martensite) are definitely less corrosion-resistant than either the martensitic or the sorbitic steels, which, in turn, represent a still further advance in the degree of agglomeration of the carbide. Drastically quenching alpha + beta brasses and subsequently reheating them to low temperatures result in the formation of an unresolvable structure, consisting

presumably of submicroscopic particles of the alpha phase disseminated in the beta ground mass (Fig. 122*b*). The alloy thus heat-treated is distinctly less etch- (corrosion-) resistant than the alloy simply quenched (Fig. 122*a*), in which practically all the copper is atomically dispersed (in solid solution) in a single phase (beta), or indeed than the alloy where the treatment is such as to produce a conglomeration of the alpha constituent into large particles.
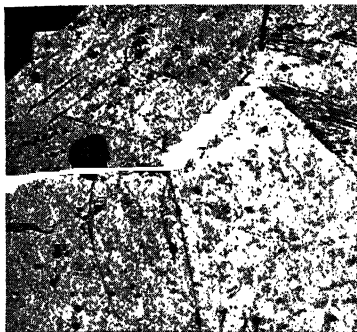
FIG. 122*a*.—Sixty per cent copper brass (Muntz metal) quenched from 840°C. The beta constituent, with some precipitated alpha in the grain boundaries. Etches with the usual 100 ×.
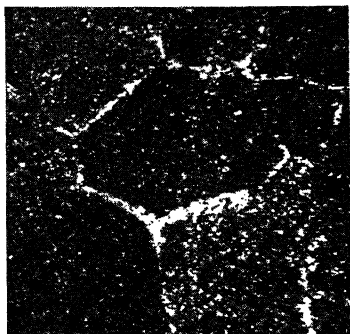
FIG. 122*b*.—Same as Fig. 122*a*, but reheated after quenching to 250°C. for 2½ hr. The unstable beta solution of the quenched alloy has broken down, precipitating the alpha phase in a finely dispersed state. Darkens rapidly on etching. 100 ×.

With such dispersed conglomerates as troostite, duplex brasses, etc., we are dealing fundamentally with the effects of structural heterogeneity on corrosion—effects, however, which are complicated by the factor of particle size. Apparently an extremely small particle size of a constituent of a complex is of consequence because the total superficial area of the discontinuous phase is out of all proportion to its total mass.

There is a rather widely observed tendency for precipitates to segregate in or near the grain boundaries, either because the dissociation of the parent solution is most rapid in these areas or because the regions immediately adjacent to the crystallite interface are more "open," offering less effective resistance to atom diffusion and thus to particle coalescence. Thus originates a

particularly pernicious form of corrosive attack—intercrystalline corrosion, where the corrodent concentrates its efforts on these particular vulnerable areas. The metal becomes eventually honeycombed, a condition less discoverable by appearance or weight loss than by decrease in ductility and tenacity. Duralumin—an age-hardening aluminum alloy—is less corrosion-resistant if aging occurs at 250°C. than if it takes place more slowly at ordinary temperatures, conceivably so because in the higher temperature-aged alloy (diffusion having been more active) some grain-boundary segregation of the precipitate occurs. The stainless steels of the 18 (chromium)-8 (nickel) type, probably the best known of the noncorrodible alloys of iron, lose their stainlessness if intergranular precipitation of the carbides (of chromium, iron) occurs. This is the case in the steel whose photomicrograph is shown in Fig. 121.

Generally speaking, among the several alloy types, the solid solutions exhibit the best corrosion resistance, but for the fullest development of this property they must be homogeneous, *i.e.*, nondendritic in character, they must be inclusion-free, and in some instances they should be of definite compositions. The maximum stainlessness of the stainless steels is attained after a heat-treatment which puts into, and retains in, solid solution all chromium and carbon (and nickel). We have then a single-phase alloy. There can be no question, then, of possible galvanic activity. Tammann observed many years ago that certain definite compositions in the gold-copper and the gold-silver alloys gave best resistance. The specific compositions which proved themselves superior were those where the nobler metal constituted 12.5, 25, 37.5, etc., atomic per cent of the alloy, or where the number of atoms of the nobler metal constituted $\frac{1}{8}$, $\frac{2}{8}$, $\frac{3}{8}$, etc., of the total atoms present. These critical compositions were called "reaction limits." This circumstance explains the curious fact, known to all assayers, that it is impossible to "part" the gold from silver unless the original bead contains more than 50 per cent of silver. Apparently, there is some connection between the fact of "reaction limits" and the tendency to form symmetrical solid solutions, since both conditions are found only at definite atomic percentage compositions, and both are manifest only after prolonged heating. It would appear that some specific geometrical grouping is responsible for both and

that a symmetrical solid solution permits of a better "coverage" of the less noble metal by the nobler metal.

Any physical nonuniformity is likewise conducive to lowered corrosion resistance. A localized strain-hardened area, as that existing immediately surrounding punched rivet holes in boiler plate, is anodic to more distant, unstrained areas. Corrosive attack starts in this deformed portion, then spreads elsewhere. Annealing to permit the deformed metal to recrystallize remedies the situation. A curious variant of strain corrosion is the phenomenon known as "season cracking." The breach ends of large-size cartridge cases (made of alpha brass) are formed by a cold-heading operation. Furthermore, the circumferential surface of the central primer hole is cold-swaged to size. The purpose of both operations is to provide the necessary strength in the head, and to secure a wear resistance on the hole surface sufficient to allow several replacements of the primer without an undue increase in the diameter of the hole. Cartridge cases so made, on storage in humid, tropical climates for several months, may develop a series of radial cracks in the breach head. The cartridge case may even split throughout its entire length. The appearance of the radially cracked head closely resembles that of the end of a well-seasoned log, whence has come the name of the phenomenon. The cracking results from the slow action of a mild corrodent on the alloy which has some residual internal strains from the manufacturing operation. Traces of ammonia and other nitrogen-bearing gases in the atmosphere, resulting from the evaporation or decomposition of organic substances, are particularly effective.

The cure for the condition is to render the article immune from attack by removing the residual strains. A short-time (flash) anneal is usually sufficient, yet at the same time results in no appreciable letdown in the hardness. The test for season-cracking susceptibility illustrates an interesting instance of inter-crystalline attack. Moreover it is an exaggerated case of an accelerated corrosion test. The finished article is immersed in an aqueous solution, of the proper concentration, of a mercury salt. Copper enters the aqueous solution, the replaced mercury attacks the metal surface and works its way, at a surprisingly rapid rate, along the grain boundaries below. The cohesion between the alpha grains is thereby lessened, in severe cases,

totally destroyed. The presence of residual stresses from a cold-working operation in such a weakly cohering aggregate causes cracking and, in extreme cases, complete disintegration of the article. This may take only a few minutes, if the internal strain is of any consequence at all. The test is obviously a destructive one and its value is, of course, principally in developing a manufacturing technique whose products shall be immune from this defect.

The effect of temperature on corrosive attack is to be expected from the known behavior of chemical reactions with increase of temperature. The resistance of a metal at higher temperatures is decreased because the activity of the corrodent is greater. In some cases the accelerating effect of temperature on corrosion is partly directly traceable to the metal itself; it actually becomes less resistant. This is particularly true in those alloys where the so-called reaction limits are found. The ennobling effects of these critical compositions disappear at high temperatures, seemingly because the increased kinetic energy of the noble atoms, by reason of the high temperature, causes them to be less permanently secure in their sentry positions.

Always a determining factor in corrosion is the character of the corrosion product. If a piece of iron or mild steel is immersed in dilute nitric acid, it becomes immediately attacked, and the attack continues so long as either the metal or the acid is present. If, however, the metal is immersed in a more concentrated acid, *e.g.*, one which has a specific gravity of about 1.3, the attack which is rather vigorous at first soon abates and may even cease altogether. With still higher concentrations of acid, (specific gravity, 1.42), there is no apparent attack at all. Immersion in acid of this high concentration has made the metal "passive." This immunization, as far as this particular corrodent is concerned, is seemingly permanent. With respect to other corrodents, particularly those which do not themselves produce passivity (*i.e.*, are not oxidizing), the condition is temporary. The cause of passivity is the formation of an impervious film of oxide (ferric oxide, in this case), of not more than 0.00005 mm. in thickness (Evans). This investigator observed the existence of such a film on metal that had been merely exposed to air for a short time.

If the corrosion product forms an impervious, continuous, and closely adhering film over the surface attacked, the metal under-

neath is permanently protected. The metal chromium added to iron or to mild steel produces passivity effects, supposedly because the protective film resulting is a much more stable one than the film that forms on chromium-free iron. Any constituent, or enclosure, like carbides in steels, which breaks up the continuity of the oxide film, decreases the latter's efficiency as a protective coating. Also, in the case of carbides in steels, the fact that they are electronegative to ferrite results in the latter being attacked, thus undermining the protective film.

Bronzes (copper-tin alloys) and the tin-bearing brasses exhibit considerable resistance to salt-water corrosion, which is one of the most active of corroding processes. The passivity of these substances is supposedly due to the early formation of a protective film of a stable tin chloride. Lead and other metals and alloys are similarly protected by a corrosion-product film. In other cases, the corrosion product is either chemically unstable or physically such that it affords no real protection. The product of the rusting of iron—iron rust—belongs to this category. It is ordinarily a voluminous powder, variable in composition, and giving no protection because it does not adhere tightly to the place of its origin. Moreover, it is not impervious to moisture; actually it may facilitate corrosion through its absorption of moisture.

With respect to natural corroding agencies, we may distinguish three: air, water, and soils. These differ from each other, perhaps not so much in the fundamental mechanism of attack as in the rate and severity of dissolution and disintegration of a given material. Each general corroding medium is, in reality, a complex system, involving in each instance such factors as:

a. Air: Whether inland or shore (salt spray); presence of smoke and industrial gases (SO_2, H_2S, CO_2, etc.); humidity, temperature, wind velocity, etc.

b. Water: Fresh or salt, purity (dissolved substances from soil, air, etc.); industrial wastes; flowing or stagnant; presence of suspended matter; bacteria and other marine organisms.

c. Soils: Composition (alkaline, saline, sulphurous, decomposing organic matter, etc.); physical texture; ground water composition and seasonal fluctuation of ground level; electrolysis caused by stray underground currents; plant life.

The practical significance of so large a number of possible variables in any one of the three natural environments is (1) the

impossibility of anticipating with any feeling of confidence in one's conclusions what the behavior of a given alloy will be when it is exposed to the atmosphere, immersed in water, or buried in the soil, except as one's expectations are based on evidence derived from previous experience with the actual conduct of the alloy in service under supposedly identical conditions; (2) the futility of expecting to simulate in the laboratory the often hopelessly involved conditions surrounding corrosive attack in nature, and the questionable worth of laboratory results obtained when such conditions are not faithfully duplicated; and (3) the unlikelihood that a single alloy will have its corrosion-resisting powers so generalized and catholic that it is equally invulnerable to all sorts and conditions of corrosive attack.

The demands of modern chemical technology are no less exacting, with respect to corrosion resistance, than is nature itself, but the corroding conditions are more often known and are more accurately reproducible in laboratory tests.   The heavy chemical, paper, soap, paint and pigment, nitrogen-fixation, pharmaceutical, and the dye and organic-chemical industries—to mention a few—require corrosion-resistant materials for containers and apparatus used in the manufacture, storage, and transfer of corrosive liquids peculiar to each industry.   The corrosive conditions encountered in some of these manufacturing processes may be made more severe by reason of the high temperatures employed.   The cleansing, dyeing, and laundry industries are also important users of corrosion-resistant metals. This is also true for those industries interested in the preparation and manufacture of food products—the sterilization and distribution of milk and other alimentary liquids, the manufacture of edible oils, and the preparation and preservation (canning, desiccation, refrigeration) of fruits, vegetables, meat, and fish. In most of the latter cases, it is not only a question of securing a reasonably long life in a container, conveyor, or machinery part, but the possibility of contamination of product may be of greater weight in the choice of what material to use.

A short list of noncorroding metals and alloys follows.   It should be remembered, however, as the corrodibility of a metal is so often a question of a particular corrodent, that with respect to some media any of the alloys listed might possess little merit.

1. Absolutely pure metals and the commercially pure noble metals.

2. Noble-metal alloys of high fineness.

3. Alloys of iron, of low or no carbon content, with chromium, or with chromium and nickel.

4. Alloys of iron with high silicon.

5. Nickel alloys of high nickel content with iron, chromium, and copper.

6. Complex chromium, nickel, silicon, molybdenum, tungsten, and iron alloys containing three or more of these metals.

7. Cobalt alloys with chromium or chromium and tungsten.

8. Nitrogen-surfaced steels.

9. Nontarnishable (stainless) alloys, as the noble metals and their alloys, the stainless steels of the 18-8 or the cutlery type, German silvers, austenitic steels, etc.

Three groups of useful, noncorroding alloys of chromium, iron, and nickel are shown in a three-dimensional plot in Fig. 123.
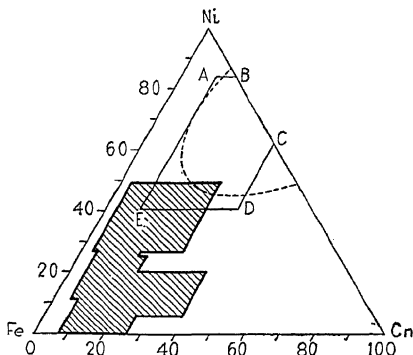
Fig. 123.—Corrosion-resistant alloys of iron, nickel, and chromium.   Shaded area = stainless irons; curved area = nichromes; area $ABCDE$ = turbine blade alloys (German).   (*After Monypenny.*)

b. **Heat Resistance.**—Heat resistance implies (1) resistance to oxidation, and other reactions, at high temperatures; (2) structural stability at high temperatures; and (3) the retention of adequate mechanical properties at high temperatures.

It has been stated above that a very thin, invisible film of ferric oxide is found on iron which has been exposed to air at ordinary temperatures for a short time.   As the temperature rises, the thickness of the film increases, at first becoming thick enough to become visible through interference effects, then becoming definitely opaque and taking on a scalelike character. The circumstance that the film increases in thickness with

temperature indicates that the film first to form is not sufficiently protective in preventing further oxidation. Apparently, it is either porous, or nonadherent, or both; in any case no really adequate protection is afforded by its presence, and oxidation of the metal below goes on apace.

When the hardenable 12 per cent chromium stainless steels were first used, it was noted that they scaled less badly during heat-treatment than did the plain carbon steels, obviously because the initially formed oxide film did effectively exclude the oxygen from the metal underneath. At temperatures up to 800°C., or thereabouts, little scaling of these steels occurs, but above oxidation becomes active. At these higher temperatures, protection ceases, apparently through some change in the character of the film. It may become less stable chemically, or less impervious; certainly it becomes less adherent, for the alloy now freely scales.

TABLE 12.—WEIGHT INCREASES (MG./SQ. CM. OF SURFACE AREA) OF STEELS WHEN HEATED IN AIR FOR 24 HOURS

(After Hatfield)

Temperature, °C.	Mild steel (0.17% carbon)	Cr steel (0.32% carbon; 13.12% Cr; 0.29% Ni)	Cr-Ni steel (0.12% carbon; 17.74% Cr; 8.06% Ni)
100	nil	nil	nil
200	0.03	0.01	nil
300	0.13	0.04	0.02
400	0.45	0.08	0.04
500	0.62	0.09	0.04
600	4.64	0.20	0.13
700	11.92	0.40	0.22
800	44.92	0.77	0.40
900	57.17	1.07	0.46
1000	135.78	66.67	21.82
1100	208.00	165.27	72.30
1200	399.88	261.00	177.66

A comparison of the relative scaling resistances of a plain carbon steel, a chromium steel, and a chromium-nickel steel of the 18-8 type is given in Table 12. The figures represent increases in weight due to the formation of the oxide scale. It will be noted that in the case of the two alloy steels the weight

increases due to scaling are not appreciable until temperatures
of 1000°C. are reached, while scaling of the carbon steel is active
at 700°C.

TABLE 13.—EFFECT OF VARYING ATMOSPHERES ON THE RATE OF
OXIDATION OF A 0.17 PER CENT CARBON STEEL AT 900°C.
(After Monypenny)

Atmosphere	Increase in Weight (Mg./Sq. Cm. of Surface)
Pure air	55.24
Atmosphere	57.17
Atmosphere + 2% SO_2	65.76
Atmosphere + 5% SO_2 + H_2O	152.42
Atmosphere + 5% CO_2 + H_2O	100.44

TABLE 14.—EFFECT OF VARYING CHEMICAL COMPOSITION OF STEEL ON
ITS CORROSION RATE AT 900°C. IN A FURNACE[1]
(After Monypenny)

Composition					Increase in weight (mg./sq. cm. of surface)
C	Si	Cr	Ni	W	
0.17	0.18	.....	0.25	....	73.10
0.50	3.04	8.28	0.16	....	0.51
0.09	0.37	18.53	0.26	....	1.38
0.11	0.21	14.84	10.16	....	3.84
0.12	0.31	17.74	8.06	....	0.33
0.35	0.21	10.90	35.14	....	1.01
0.24	0.16	0.09	36.90	....	27.70
0.58	4.00	15.54	8.14	....	0.06
0.30	1.46	17.74	7.00	4.23	0.18
0.06	0.71	11.69	60.40	....	0.77

[1] Analysis of furnace atmosphere: N 67.7 per cent; O 1.34 per cent; CO_2 4.75 per cent; steam 21.10 per cent; SO_2 0.003 per cent; and CO 5.10 per cent.

The effects of the chemical composition of alloy and of the
atmosphere on corrosion may be seen in Tables 13 and 14. The
results of Table 13 show that atmospheres containing considerable
quantities of either SO_2 or CO_2 are more corrosive than air free
from these two anhydrides. Monypenny has further sum-
marized the effects of special elements in steels on corrosion
resistance at high temperatures (supporting data are only incom-
pletely shown in Table 14) as follows:

1. Chromium is the chief agent in promoting resistance to oxidation; the amount of this metal required in iron chromium alloys to give protection at various temperatures is approximately 15 per cent for temperatures up to 850°C., up to 30 per cent for temperatures as high as 1150°C. The respective values are not affected appreciably by the presence of 8 or 10 per cent nickel in the steel.

2. A high nickel content, *e.g.*, 20 per cent or more, increases the protection afforded by a given amount of chromium to oxidation by air, oxygen, steam, or carbon dioxide. A high nickel content, however, is not useful if resistance is desired at high temperatures to gases containing sulphur dioxide or other sulphur compounds.

3. Small additions of silicon or aluminum, *e.g.*, 1 or 2 per cent, increase very markedly the resistance of high chromium steels to oxidation.

4. The presence of 3 or 4 per cent tungsten in chromium or chromium-nickel steels does not appear to increase the resistance to oxidation.[1]

Stainless steels are not the only heat-resisting alloys, nor are they the oldest. Previous to their introduction, the carbon-free alloys of chromium and nickel (nichromes), and of iron, chromium, and nickel had been long employed for this purpose. These alloys are still widely used. In addition to high scaling resistance, they have a low electrical conductivity and a very low temperature coefficient. They have long been used as electrical-resistor units. They seem ideal for this purpose since in addition to the desirable electrical properties mentioned, a prolonged exposure to high temperatures does not unduly decrease their cross-sectional area through scale formation.

For many high-temperature uses, a certain degree of internal structural stability is required in an alloy, as well as an external passivity. Grain growth on long exposures to high temperatures, and other structural alterations incident to heating to, and cooling from such temperatures are cases in point. Grain growth in stainless steel, for example, depends in addition to the effect of temperature, *per se*, on the temperature of the alpha $\leftrightarrows$ gamma transformation (which in turn is a function of the chromium and nickel contents), for the ferritic grains grow rather more actively than do the austenitic ones. Grain growth here, as in other cementitic steels, is also dependent on the amount of the obstructing carbides.

[1] MONYPENNY, J. H. G. "Stainless Iron and Steel," 2d ed., p. 421, 1931.

The general effect of change in mechanical properties with temperature has already been discussed in an earlier section. In Fig. 124 are given the comparative high-temperature strengths of a hardened stainless steel (12 per cent chromium) and of two similarily treated carbon steels. The superiority of the chromium steel in strength properties at high temperatures is apparent. We should expect, therefore, that the creep strength of the stainless steel would exceed those of the simple carbon varieties, and this is indicated in the plotted values of Fig. 125.

c. Diffusion in the Solid State.— Chemical likeness in all its parts is characteristic of any solution, and the solid variety seems no exception. But quite otherwise may be the fact, as is commonly the case when an alloy solidifies under the usual nonequilibrium-attaining, selective freezing procedure of solid solutions. In these heterogeneous solutions, the urge for uniform distribution, on the part of the solvent and the solute atoms, becomes realized only when circumstances are favorable for diffusion. The normal rigidity

FIG. 124.—Tensile strength of hardened steels at temperatures up to 600°C. *A*, stainless steel (12 per cent chromium); *B*, one per cent carbon steel; *C*, one-half of one per cent carbon steel. (*Afte Monypenny.*

of the lattice at ordinary temperatures effectively prevents an atomic migration sufficient to bring about homogeneization. However, if the chemically heterogeneous, dendritically segregated solid solution is subsequently heated for a sufficiently long time, at a temperature somewhat below its melting point, diffusion can occur, and eventually the alloy will become chemically uniform.

If two metals (or a metal and an alloying nonmetal), which normally form solid solutions with one another, are placed in intimate contact, and heated, it will be found that atoms of the one will have passed into the lattice of the other. This is another instance of diffusion in the solid state and, like the homogeneiza-

tion of "as-cast" solid-solution alloys, forms the basis of many industrially important processes.[1]

The migratory behavior of atoms within a lattice, seeking lower concentration levels, more especially their diffusion rates, is influenced by two groups of factors: (1) those which concern solubility, and (2) those which determine the "looseness" of the solvent lattice. Under Group I are included such influencing factors as the extent of solid solubility, the type of solid solution forming, and the relative size of the solvent and the solute atoms. It is an obvious prerequisite of diffusibility in the solid state that the atoms concerned belong to metals that form solid solutions with one another. An atom must be part of the lattice structure occupying either points thereon or positions within—before it can move about through the lattice. When there is no appreciable solid solubility, any migratory movement must be confined to the grain boundaries.

FIG. 125.—Stresses producing creep of 1 in 10^6 per hour.   (*After Norton.*)

Curve	Carbon	Silicon	Chromium	Nickel	Tungsten
A	0.8				
B	0.20				
C	0.34	0.17	.....	.....	0.74
D	0.10	0.86	17.6		
E	0.09	0.43	18.11	8.12	
F	0.14	1.09	6.37	19.01	

The marked diffusibility of the relatively small, interstitially placed carbon atoms in gamma iron has already been referred to. On the other hand, we find the absorption of carbon by alpha iron to be extremely slow. This is apparently due to the low solubility of carbon in the low-temperature modification of iron.

The factors of the second group that may influence diffusibility are those which have some influence upon the physical character of the lattice, *i.e.*, upon its openness or "looseness." At room temperatures, the lattice is ordinarily a rigid affair, and a wandering atom makes little or no headway. As the temperature is increased, the kinetic energy of the atoms on the lattice

[1] For example, carburizing (introducing carbon into the surface of a mild steel); nitriding (introducing nitrogen into the surface of certain steels); sherardizing (introducing zinc into the surface of iron); and calorizing (introducing aluminum into the surface of iron).

positions becomes greater and their oscillations (thermal) assume a wider amplitude. As a consequence, the possibility of shift in positions becomes real. Diffusion may then occur with considerable rapidity.

Cold deformation also increases the diffusion rate, probably because it, too, disturbs or "loosens" the lattice through the distortion produced. In such a loosened lattice, atomic interchange is made easier.

Grain size is also of some consequence in determining diffusion rate, with the faster rates found in the finer grained aggregates. The grain-boundary effect is perhaps again associated with the assumed more open lattice in the grain-boundary regions. Some such condition has been suggested to explain grain-boundary segregation of precipitates, such as occurs, for example, in certain heat-treated stainless steels.

Some recent work indicates that when two metals are in close contact, atomic migration proceeds from the metal whose "interatomic distances" are smaller to that whose "distances" are larger. In Table 15, are given the results of this study.

TABLE 15.—DIFFUSIBILITY DIRECTIONS IN SOME METAL PAIRS

Metals	Minimum interatomic distance, cm. $\times 10^{-8}$	Direction of diffusion
Cu-Pt	Cu 2.54 Pt 2.78	Cu penetrates Pt
Fe-Ag	Fe 2.54 Ag 2.876	Fe penetrates Ag
Au-Pb	Au 2.88 Pb 3.48	Au penetrates Pb
Fe-C	C 1.50 Fe 2.54	C penetrates Fe

III. Physical Properties.
    1. Electrical conductivity.
    2. Thermal conductivity.
    3. Magnetic properties.
    4. Thermal expansion.
    5. Color.

Electrical Conductivity.—The conductivity of alloys is generally inferior to that of the pure metals; the variation of this property with composition, for the several types of solidification

procedures, is given in Fig. 126. Alloys of the solid-solution type of structure, because of the latter's abnormally high resis-
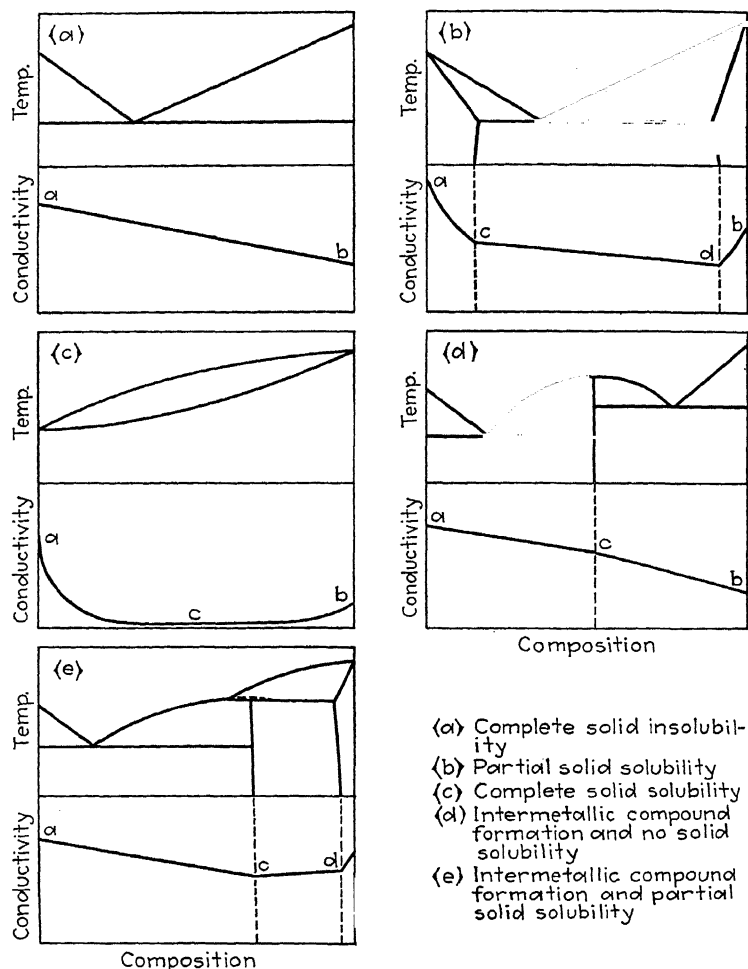
FIG. 126.—Electrical conductivity curves in relation to constitution.

(a) Complete solid insolubility
(b) Partial solid solubility
(c) Complete solid solubility
(d) Intermetallic compound formation and no solid solubility
(e) Intermetallic compound formation and partial solid solubility

tivity effects, are the alloys of interest. The introduction of stranger atoms in the host lattice severely curtails the "freedom" of the electrons supposedly responsible for electronic conduction.

It also makes such conduction less dependent on temperature, for the temperature coefficient of resistance of solid–solution alloys is invariably low. The temperature coefficient vs. compo-
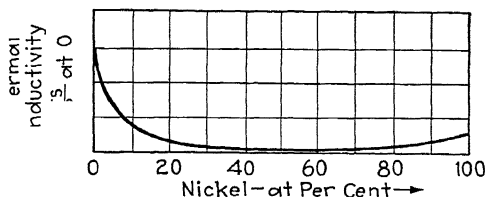
Fɪɢ. 127.—Thermal conductivity of the copper-nickel alloys as calculated from thermoelectric measurements by Sedstrom.

sition curve of an isomorphous-solution series is, like the conductivity vs. composition curve, a broad U-shaped affair. The particular solid-solution alloys that have proved especially useful technically, not only because of their inherently high resistivities, but also because of their superior heat-resisting properties, are alloys of the metals chromium, nickel, and iron. Some of these alloys, with their specific resistances and their temperature coeficients, are given in Table 16.

The electrical conductivity of a solid solution is a function, as we recall, of the composition (Fig. 128); it is also dependent on the heat-treatment, if superstructural tendencies are present or if the solid solution is age-hardenable by reason of supersaturation. (See Fig. 133c.) The addition of a soluble third metal to a binary-solid solution will result ordinarily in a further increase in the resistance.
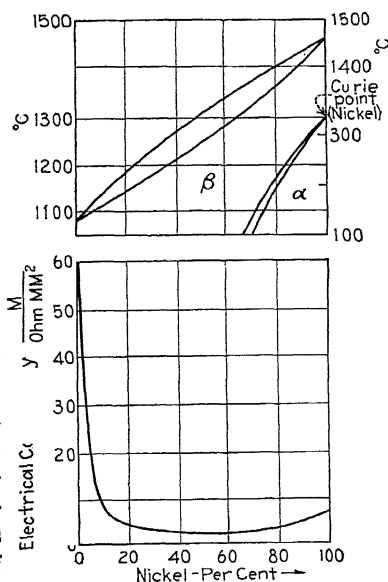
Fɪɢ. 128.—Equilibrium diagram, and the electrical conductivity of the copper-nickel system.

Thermal Conductivity.—Like its electrical counterpart, thermal conductivity is most influenced by solid-solution formation. The similarity between the two conductivity curves (compare Fig. 127 with Fig. 128) is striking.

Magnetic Properties.—Magnetically, substances may be divided into two groups: those (called paramagnetic) which are more permeable than air to magnetic lines of force, which concentrate such lines as pass through them and which, themselves, become aligned parallel to a nonuniform magnetic field; and those (diamagnetic) which are less permeable than air, disperse the lines of force, and assume a position normal to the field.   Three

TABLE 16.—ELECTRICAL-RESISTANCE PROPERTIES OF SOME CHROMIUM-NICKEL ALLOYS

Composition				Specific resistance $\left(\dfrac{\text{ohm sq. mm.}}{\text{m.}}\right)$	Temperature coefficient of resistance (200–1000°C.)
Cr	Ni	Fe	Mo		
11	89	. .	. .	0.85	0.000200
15	85	. .	. .	0.95	0.000061
20	80	. .	. .	1.10	0.000058
15	63	22	. .	1.11	0.000117
20	70	10	. .	1.08	0.000091
25	65	10	. .	1.10	0.000076
33	50	17	. .	1.05	0.000227
15	53	15	7	1.20	0.000056

elementary substances of the paramagnetic group—iron, nickel, and cobalt—are abnormal in their magnetic properties[1]; they and certain of their alloys and, curiously enough, another group of alloys containing no one of the three constitute a special case of paramagnetism, known as *ferromagnetism*.   Iron and nickel lose their ferromagnetic properties when heated to a sufficiently high temperature and become simple paramagnetic bodies.   This magnetically critical temperature (the Curie point) is 768°C.

[1] The factor of permeability (μ), (conventionally taken as equal to unity for air, is less than unity for diamagnetic bodies and greater than unity for paramagnetic bodies) is constant, *i.e.*, independent of the strength of the magnetizing field, except in the case of ferromagnetic substances.

for iron and 368°C. for nickel. The transformation temperature is affected commonly by alloying (see Fig. 128).

The ferromagnetic metals and alloys, in turn, may be divided into two general classes: those magnetically soft, and those magnetically hard—a property distinction that may most readily be clarified by a comparison of the characteristics of the magnetization cycles of the two groups. Two such curves, one of a magnetically soft and another of a magnetically hard material, respectively, are given in Fig. 129. Each curve is a plot of the magnitude of the magnetism, the so-called flux density (B),

(a) Magnetically soft.   (b) Magnetically hard.
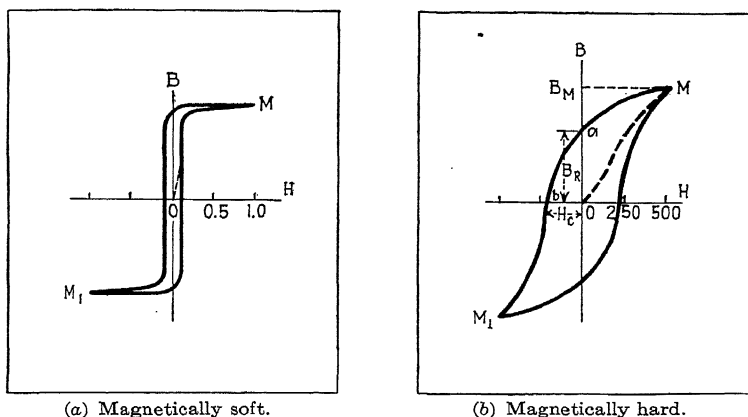
FIG. 129.—Schematic representation comparing characteristics of magnetically soft and hard materials. (*After Ellis and Schumacher.*)

induced in the magnetic material vs. the strength of the exciting magnetic field (H). The former quantity is measured in oersteds, and the latter in gauss.

The distinctive differences between a magnetically soft and a magnetically hard material, as is manifest by a comparison of their hysteresis loops, are: the smaller loop area of the soft material, indicative of the lower energy (heat) losses sustained when the latter material undergoes repeated cyclic changes; the steeper slope (B/H values) of the magnetization curve of the softer material, revealing the latter's greater initial permeability; and the lower coercive force of the soft material which is a measure of the retentivity (the tenacity with which the residual magnetism is held).

The physical metallurgist's interest in magnetic properties comes about through the circumstance that these properties are influenced by chemical composition, by physical constitution, and by thermal and mechanical treatment. Let us first consider the magnetically soft group of ferromagnetic materials. Of importance here are: pure iron, alloys of iron and silicon, of iron and nickel, and of iron and cobalt.

1. Magnetically Soft Alloys.   *a. Iron and Iron-silicon Alloys.* The magnetization characteristics of a single crystal of iron are given in Fig. 130*a*. Obviously, for moderate field strengths at least, the ease of magnetization of such a crystal is not altogether an isotropic property.

The alloying elements inadvertently present in iron of commercial purity, which are of greatest influence on the magnetic properties of iron, are those which are interstitially soluble, in particular carbon, oxygen, and nitrogen. These are most completely removed by a high temperature (above 1300°C.) annealing in a hydrogen atmosphere. A much older but generally less effective method of improving the magnetic softness of iron is the addition of silicon in amounts of about 4 per cent. Silicon enters the iron lattice substitutionally, and this mode of solution is evidently much less destructive of the permeability properties of the iron than is the alternative solution method; moreover the presence of silicon in the lattice apparently lessens iron's solubility for carbon, while the deoxidizing powers of silicon aid in the removal of the dissolved oxygen. Altogether the effect of silicon on magnetic softness is a decided one (see Fig. 130*b*). Mild steel, containing about 4 per cent silicon (electrical sheet), is a widely used material of the electrical machinery industry (for alternating-current machinery).

b. Iron-nickel Alloys.—Two compositions are magnetically and metallographically interesting: the 25 per cent and the 78 per cent nickel alloys. The 25 per cent nickel alloy occurs around the composition which shows maximum hysteresis in the $\gamma_{\text{paramag.}} \rightleftarrows \alpha_{\text{ferromag.}}$ change on heating and cooling. On cooling this alloy from the gamma field, the $\gamma \rightarrow \alpha$ change is not complete until temperatures somewhat below room temperature are reached; on reheating the completely transformed, *i.e.*, ferromagnetic alloy, the reverse $\alpha \rightarrow \gamma$ change is not fully accomplished until· about 600°C. In other words, the alloy is either ferro-

magnetic or not at temperatures within the hysteresis gap, depending upon the direction of approach. If this be from above (on cooling), the alloy will be nonmagnetic; if from below (heating), it will be magnetic. This has been called an "irreversible
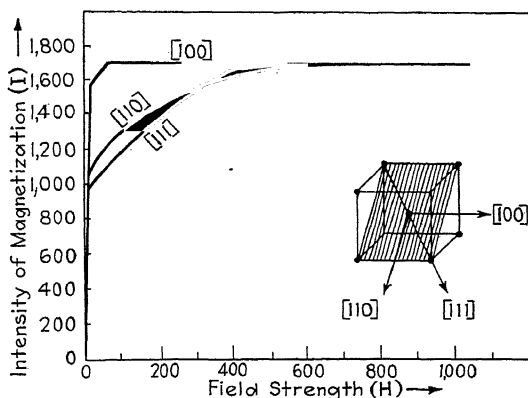
Fig. 130a.—Magnetization curves of a single crystal of iron. (*After Honda and Kaya.*)

alloy," but the behavior of the alloy is not precisely so; it does really reverse itself, but at a temperature distance which, from one's knowledge of the magnitude of other hysteresis effects, would be considered unusually far.
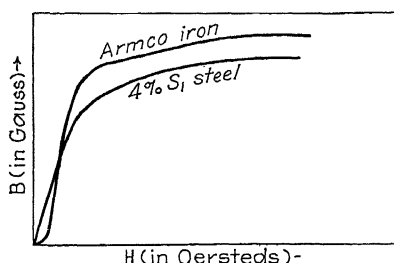
Fig. 130b.—Magnetization curves of a commercially pure iron and 4 per cent silicon steel. (*After Ellis and Schumacher.*)

The 78 per cent nickel alloy—one of the group of the "permalloys"—has an extremely high initial permeability. The magnetization curves of this alloy, in two heat-treated conditions, and—for comparison purposes—that of a commercially pure iron

(Armco) are shown in Fig. 131. The 78 per cent alloy is also interesting metallographically because of the circumstance that
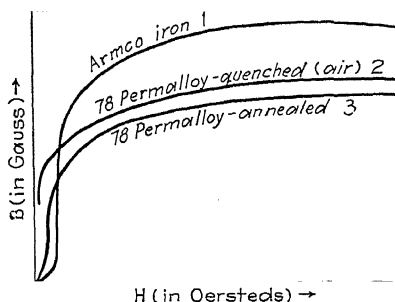
Fig. 131.—Magnetization curves of Armco iron and 78 per cent nickel Permalloy. (*After Elmen.*)

its magnetic softness is susceptible of modification by heat-treatment. In Fig. 132 is given the relationship between the
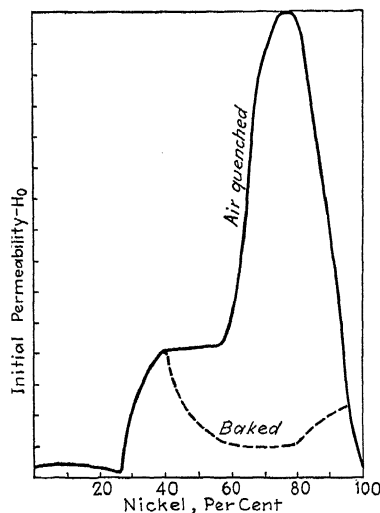
Fig. 132.—Effect of heat-treatment on the initial permeabilities of iron-nickel alloys. (*After Elmen.*)

initial permeability and composition of the iron-nickel alloys. Two different heat-treatments are also shown here: air quenching from above 500°C., and a very low temperature anneal (bake). The marked disparity in permeability values resulting from so simple a variation of thermal treatment of a non-polymorphic solid solution as is shown here in the case of the 78 per cent alloy, seems highly evidential of a distinct difference in the fundamental fine structure of the two alloys. The circumstance that the maximum property difference is associated with a single narrow composition range—the 75 to 78 per cent of nickel range, where the ratio of the number of iron to nickel atoms is 1:3—suggests, as pointed out by Elmen, and by Ellis and Schumacher, that

symmetrical solid solutions (superstructures) form in the series "somewhere around 500°C." Heating the alloy above 500°C., followed by rapid cooling, preserves the random distribution of the two atom species on the basic lattice, while an annealing below this temperature, if of a sufficient duration, permits the atoms to arrange themselves in a certain symmetrical fashion, with disastrous consequences to the permeability of the alloy. Other physical properties, such as the electrical conductivity and the tensile strength, are likewise affected by the same heat-treatments.

Heusler Alloys.—Strangely enough, this group of ferromagnetic alloys contains no one of the ferromagnetic metals. These alloys are nominally manganese-aluminum-copper alloys, with the manganese essential and the copper and aluminum replaceable by elements of like valence. The ferromagnetic properties of the alloys are associated with the composition where the number of atoms of copper, manganese, and aluminum is in the ratio of 2:1:1. Quenching from above 800°C. is necessary. Here, again, superstructure formation is involved.

2. Magnetically Hard Alloys.—These materials are used for the manufacture of permanent magnets and are characterized by a high residual magnetism (B_r) and a high coercive force (H_c). In a permanent-magnet material, not only does one want a large part of the induced magnetism retained after the magnet is removed from the magnetizing field, but one desires also that this residual magnetism will be preserved under any and all conditions that the magnet may meet in service. In Table 17 is given a list of some alloys which after suitable heat-treatment are sufficiently hard magnetically to be used for permanent magnets.

The heat-treatment given to the permanent-magnet steels, as those in Table 17, is to quench them from above the temperature where the gamma phase (of iron) is the stable one, and in which all of the carbon is in solid solution. The cooling (quench in water or oil) is not fast enough to prevent the gamma iron transforming to the alpha condition, in which, as we know, carbon has slight solubility. The carbon is thus precipitated at the time of the transformation, during the quenching, as discrete carbide (of tungsten, chromium, iron) particles, finely dispersed throughout the alpha-iron matrix. This critical carbide dis-

persion prevents changes in the magnetic condition from readily occurring. The quenched steel is magnetically hard, just as it

TABLE 17.—COMPOSITION AND PROPERTIES OF SOME PERMANENT MAGNET STEELS[1]

No.	Composition						Magnetic characteristics		
	C	Cr	W	Co	Mn	Si	H_c	B_r	$H_c \times B_r \times 10^{-3}$
1	0.60	....	...	..	0.80	0.20	40	9,000	360
2	0.60	0.90	...	..	....	....	50	9,500	475
3	0.90	3.5	...	..	....	....	68	9,500	645
4	0.70	....	5.0	..	....	....	60	10,500	630
5	0.75	4.0	7.0	35	....	....	220	9,500	2,090

[1] From Ellis and Schumacher.

Heat-treatment given to secure the above properties:

Steel	Treatment
1	Quenched from 800°C. in water.
2	Quenched from 800°C. in oil.
3	Quenched from 830°C. in oil.
4	Quenched from 845°C. in water.
5	Quenched from 940°C. in oil.

is mechanically hard, and the two conditions result substantially from the same cause.
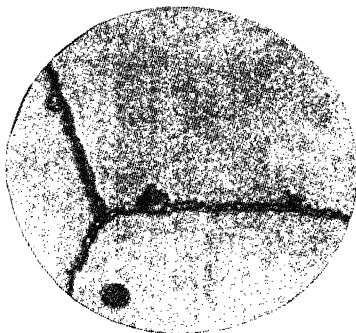
FIG. 133a.—Iron-tungsten alloy (72.1 per cent Fe and 27.9 per cent W). Quenched from 1400°C.
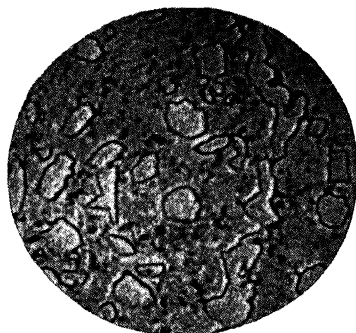
FIG. 133b.—Same alloy after aging at 1250°C. 1000×. (*Photographs by Rogers.*)

The effect of dispersion hardening on magnetic properties, but this time in *carbon-free* alloys, is shown, for example, by

Rogers'[1] work on iron-tungsten, iron-cobalt, etc., alloys. These alloys, though containing no carbon, become magnetically hard through dispersion hardening, but the dispersing process occurs subsequently to the quenching operation during a reheating of the quenched alloy to a lower temperature than the one from which the quenching took place. The initial heating (the so-called, solution anneal) has for its purpose the solution of all the solute, in this particular alloy, all of the iron tungstide; quenching is a sufficiently rapid cooling to prevent all but a very small amount (in the grain boundaries) of the tungstide from reprecipitating. (See Fig. 133a for a photomicrograph of the quenched alloy.) The quenched alloy is then reheated (the precipitation anneal) at various temperatures to cause the precipitation of the tungstide from the supersaturated solid solution. Precipitation and the formation of critically dispersed particles of the tungstide are especially active in the temperature range (for the particular time used) of 600° to 800°C., within which range of temperatures maximum changes in property values

FIG. 133c.—Physical properties-aging curves of iron-tungsten alloy (72.1 per cent Fe and 27.9 per cent W). *(Photographs and curves from Rogers.)*

occur (Fig. 133c). Higher precipitation annealing temperatures than 800°C. ordinarily result in inferior properties, supposedly because the particle size of the precipitate has now attained extracritical size. They have lost their most effective "keying" powers. A photomicrograph of the alloy in a decidedly overaged condition is shown in Fig. 133b. The tungstide particles (inclusions) are very large.

[1] Thesis, Harvard University.

Thermal Expansion.—The metals, as do all other substances, suffer dimensional changes with changes in temperature. The increase in the amplitude of the thermal oscillations with increase
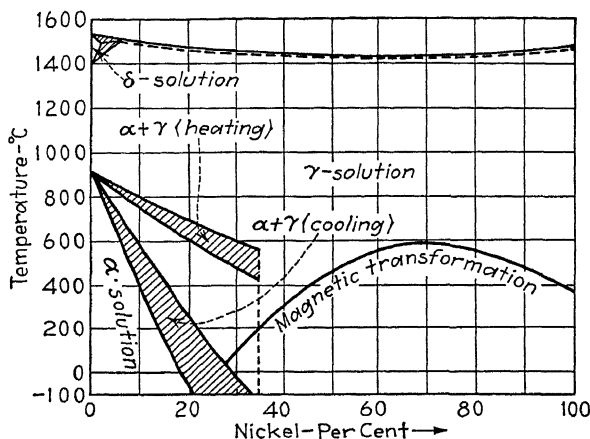
FIG. 134.—Equilibrium diagram of the iron-nickel system.   (*Ellis and Schumacher.*)

in temperature, lately mentioned as accountable for the increased diffusibility at high temperatures, may also be suspected as responsible for increasing the distances between the atoms' centers, and thus directly, the volumetric dimensions of the lattice itself.
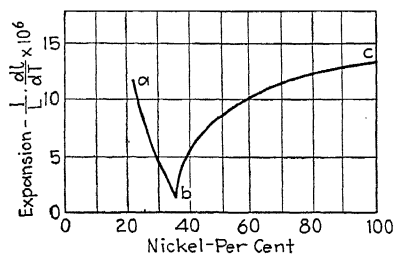
FIG. 135.—Coefficients of expansion versus composition of the iron-nickel alloys.   (*After Tammann.*)

The linear expansivity (dilatation) equation, holding for small changes in temperature, is $L = L_0(1 + at)$, where L_0 is the unit length at °C., and a is the coefficient of linear expansion.

Insufficient data prevent generalization of the effect of composition (or constitution) on the expansivity property, except possibly in the single instance of conglomerates, whose expansivity varies evidently lineally with composition. The most interesting group of alloys, from the point of view of expansion, is a solid-solution group of iron-nickel alloys. These alloys

have uniformly low expansion coefficients, and one—a 36 per cent nickel composition, known as Invar (*i.e.*, invariant)—has a coefficient, in certain ranges of temperature, that is practically nil. The volume of this alloy is, thus, independent of temperature within this range.

The explanation of expansivity so abnormally low in the 36 per cent alloy is found assumedly in the circumstance that there exists around this composition a structural discontinuity (see Fig. 134). In Fig. 135 are given the dilatation curves of compositions to the left and to the right of the critical composition. Curve *a-b* represents the dilatation changes in the iron-rich alloys with increasing nickel contents, and curve *b-c* shows similar changes in the nickel-rich alloys with increasing concentration of iron. The two curves intersect at about 36 per cent nickel, at point *b*, providing a minimum value in the dilatation-composition curve.

The coefficients of expansion of iron and nickel, and of some of their alloys, are given in Table 18.

TABLE 18.—LINEAR COEFFICIENTS OF EXPANSION OF IRON, NICKEL AND SOME OF THEIR ALLOYS

	Coefficient $\times 10^{-6}$
Iron	12.3
Nickel	11.6
Alloys, Per Cent Nickel:	
25	12.0
30	5.0
36	1.0
42	5.0
44	8.0
46	9.0
50	10.0

One use of the low-expansivity alloys, notably the Invar composition, is in parts of precision instruments, chronometers, measuring tapes, etc., whose accuracy would be affected if dimensional changes were to occur with changes in temperature. Another, perhaps more important, application of these alloys is in the manufacture of thermostatic bimetal. This is a laminated material, made by fusing together two strips of metal, one (as brass) having a normal thermal expansion, and the other being Invar. Because of the unequal expansivity on the two sides of the strip, the latter becomes bent or deflected when

heated, and in a proper device this deflection may be utilized for making and breaking an electric circuit, operating indicators, etc. The manner of deflection of four of the shapes in which bimetal may be made is shown in Fig. 136.

Color.—Color is an important property of metals and alloys that are used in the architectural and other decorative arts. The metals possess a characteristic sheen or luster, which is associated with their high degree of opaqueness. Materials reflect the kind of light which it easily absorbs; for example, a

$$t = \frac{c(T_2-T_1) L^2}{2B}$$

$$t = \frac{c(T_2-T_1) L^2}{B}$$

U-Shape

Straight Strip

$$t = \frac{c(T_2-T_1) L^2}{3B}$$

$$L = \frac{At}{c(T_2-T_1)}$$

Coils (Helix and Spiral)

Ring
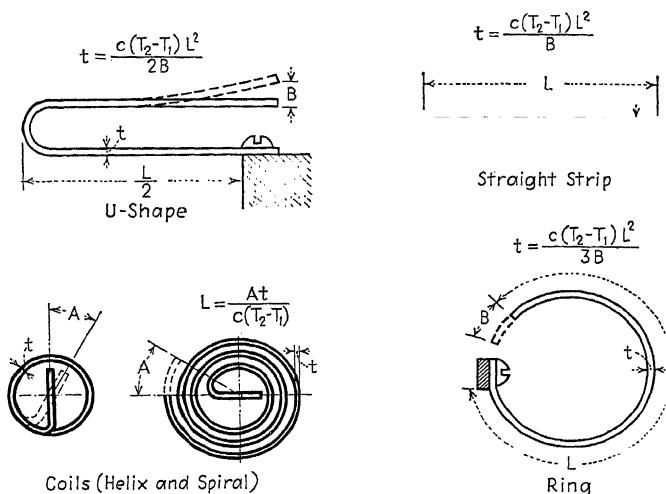
Fig. 136.—Deflectional and dimensional constants of some bimetal shapes.
(*Courtesy of General Plate Company.*)

fuchsin (dye) solution is transparent to reds and yellows, but not to greens. These are absorbed, and in the spectrum the place of green is occupied by a black band. Green is the color reflected by this dye. Gold leaf permits passage of the blue rays but effectively stops (absorbs) the yellow; this color is strongly reflected so much so that the metal *is* this particular color. The optical property of metallic luster is occasionally met with elsewhere—as the interface of air (bubbles) and water, the waxen surfaces of certain aquatic plants when immersed in water, and, as indicated, in certain dyes of complex molecular structure.

Colored alloys contain copper or gold, or both—the only colored metals. There is no information concerning structure effects on alloy coloration. To be sure, our colored alloys are, for the most part, solid solutions, but this is due to the inveterate habit of copper and gold to form solid solutions. Some intermetallic compounds, containing copper or gold, are colored; strangely, too, the color of the compound may be quite unlike that of the colored metal, as, for example, the delicate purple of the compound of copper and antimony (Cu_3Sb).
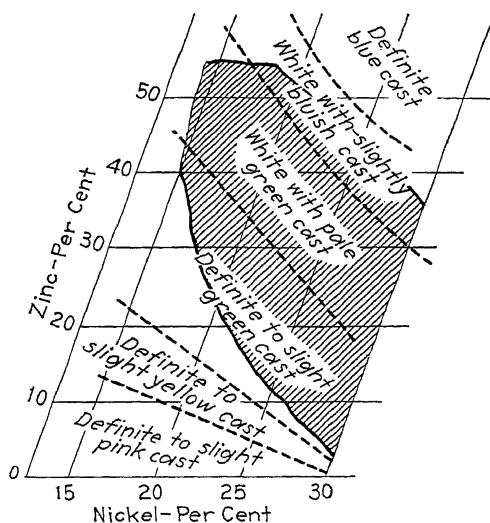
Fig. 137.—Color trends in copper-nickel-zinc alloys. Shaded area indicates sensibly "white" alloys. (*After Kihlgren, Pilling and Wise.*)

The off-coloring effects of alloying elements, used as "hardeners" in gold alloys, are an important consideration in the manufacture of these alloys. The most vigorous "whitener" is perhaps nickel. The alloy known as "white gold," a substitute for platinum, contains appreciable amounts of this metal. Some nominal compositions of gold alloys with the color trend are given in Table 19. In Fig. 137 are shown the results of a recent study of coloration in the copper-nickel-zinc alloys (nickel silver).

TABLE 19.—THE COMPOSITION AND COLOR OF SOME GOLD ALLOYS
(After Peterson)

	Alloy Composition	Color
1.	Fine gold	Yellow
2.	Gold..................... 59% Silver.................... 16% Copper................... 25%	Orange yellow
3.	No. 2 with 1% aluminum	Dark (grey) yellow
4.	Gold..................... 58% Silver.................... 28% Copper................... 14%	Greenish pale yellow
5.	No. 4 with 7% nickel	Yellow white
6.	Gold..................... 58% Nickel.................... 12% Copper................... 26% Zinc..................... 4%	White ("white gold")

CHAPTER VII

THE MECHANICAL AND THERMAL TREATMENT OF METALS AND ALLOYS

" . . . Tubal Cain his spearhead wrought
From ore he smelted with the thorn
        And cactus tree."
                                    —RICKARD.

The workability of the metals was a property known to pre-historic man, and the making of metal objects by hammering is one of the oldest of the arts. The Genesaic legend names one, Tubal Cain, seventh in descent from Adam, as the first worker in metals; other ancient literatures speak similarly of a flourishing contemporary metalworking art. But one's real assurance of the antiquity of man's knowledge and purposeful use of the property of plasticity in the metals is based on much surviving, tangible archaeological evidence. Early man's use of the property of formability was simply to give desired shapes to metal nuggets, to fashion them crudely into ornaments and implements; not until much later, one may believe, did man discover that wrought metal possesses properties somewhat different from those of unworked metal. And, of course, the fact that the property changes due to deformation are themselves the result of changes in internal structure and condition is a comparatively recent observation. The manner of plastic deformation in metals, the changes in metallic properties as a consequence thereof, and why the deforming mechanism gives the observed effects are all the concern of the physical metallurgist.

On an earlier occasion, it was stated with scant comment that the effect of any considerable amount of cold-working on the microstructure of a metal is one of distortion and fragmentation of the several granular units, and one of general strengthening and embrittlement. We wish now to inquire a little more fully into this curious phenomenon: we should like to know, for example, somewhat more specifically than the previous brief reference

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informed us, about the particular property effects produced by cold-working, and we should like to discover, if we can, what is the precise mechanism of deformation whereby such effects can be brought about. Technical interest in deformation is, of course, confined almost entirely to the cold-working of poly-crystalline metal; it so happens that it is also this particular crystalline condition on which most of the work of an investigative character has been carried out. We shall, however, consider the matter of deformation of crystals, first, by studying the way a single crystal deforms. To do this, we shall refer to the classic
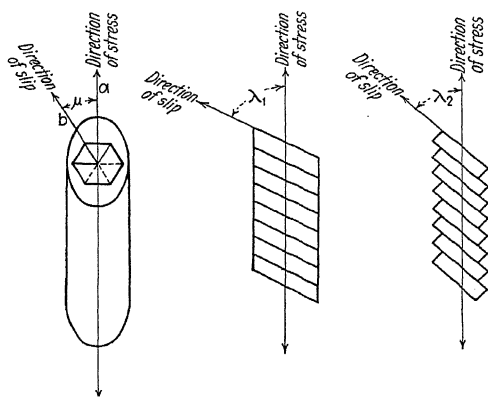
. 138.—Distortion of zinc single crystal.　(*After Elam.*)[1]

work of Mark, Polanyi, and Schmid[2] on single crystals of zinc. We recall that this metal is a hexagonal metal, described by four axes, three of which are in a plane 60 deg. to one another, with the fourth axis passing through the center of the plane and normal to it. It is observed that zinc single crystals, in wire form, are at times extremely ductile in tension, permitting extension of some four or five times their original length. On the other hand, other wires are always brittle. This variable behavior is found to be due to a difference in the position of the basal {0001} plane (which is the gliding plane of the hexagonal zinc lattice) relative to the axis of the wire. If the basal plane of the zinc crystal is neither nearly normal to, nor parallel with, the wire axis, the wire

[1] From Elam's "Distortion of Metal Crystals," Oxford University Press, by permission of the publishers.

[2] *Z. Physik*, **12**, 28 (1927).

deforms in an extremely ductile fashion. But if either of these conditions prevails, the wire is found to be relatively nonductile. Why a perpendicular position of gliding plane to wire axis should inhibit slip is apparent; why a too acutely inclined position of the axis to the plane is likewise unfavorable will be presently clear. The inclination of the gliding plane to the axis most favorable to easy slip is one of the magnitude of 45 deg. The method of gliding (plastic flow) in such a zinc single crystal is illustrated in Fig. 138. Plastic flow occurs by block movement along the gliding planes which, as has been said, are parallel to the basal plane of the metal. Steplike irregularities appear on the surface of the wire denoting where slip has occurred. Plastic flow in this crystal shows two other curious effects, both illustrated in the figure. First, the direction of slip is not the direction of greatest stress a, but is one of three directions parallel to the three pairs of parallel sides of the hexagon, specifically that direction b nearest to the direction of the maximum shear stress. As slip proceeds, the angle between the direction of maximum stress and the direction of slip (μ) becomes less; that is to say, the latter tends to become parallel with the former direction. Again, the angle between the basal plane and the axis of the wire (λ) becomes more acute with continued slip; in other words, the plane of slip as well as the direction of slip gradually rotates into the axis of tension. Obviously, the sectional shape of the wire changes during deformation, from circular to oval, *i.e.*, the wire gradually becomes a ribbon.

The deformation of a polycrystalline metal proceeds, as far as the individual crystallites are concerned, in much the same way as that described for the single crystal; *i.e.*, plastic flow takes place by transcrystalline slip. However, the freedom of any original grain of a randomly oriented aggregate to deform in its own peculiar way, immediately and continuously, to that degree of which it is inherently capable, is restricted by the circumstance that grains of different orientation and thus of different "easy-slip" characteristics, confine it on all sides. When a deforming stress is slowly applied to a polycrystalline metal, those crystals which are so oriented that some densely packed plane is favorably inclined to the direction of the applied stress are the ones first to deform. But deformation in these crystals can proceed but a little way when it is blocked by abutting

grains of an orientation different from those of the first grains to respond, and whose planes of easiest slip are not so favorably situated with respect to the direction of stress.   A higher deform-
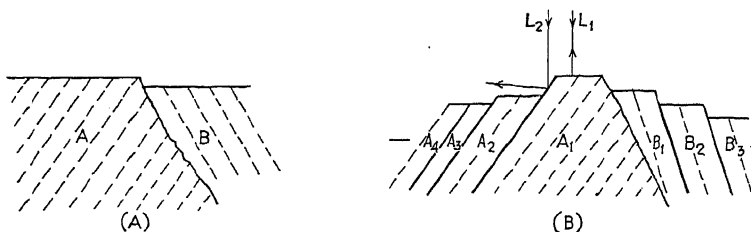
FIG. 139.—Formation of slip bands in two crystals: (*A*) the two crystals before straining; (*B*) the two crystals after straining in the direction of the arrows. A_1, A_2, etc., are portions of the original unstrained *A* grain, and B_1, B_2, etc., of the original *B* grain. L_1 represents the normal reflection of a beam of light back from the polished metal surface, and L_2 shows the path of a similar incident ray that falls on a gliding surface.   (*After Rosenhain.*)

ing load becomes necessary, if the effective resistance of the interfering neighbors is to be overcome, and if deformation of the more obstinate grains is to occur.   The bolstering effect of

(*a*) 100×.   (*b*) 500×.
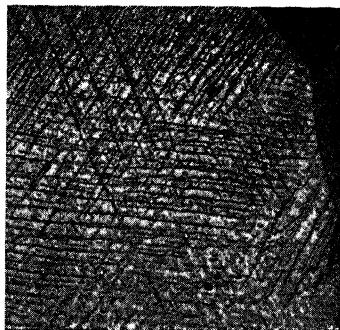
FIG. 140.—Microstructure of cold-worked copper-zinc alloy (alpha brass). (*a*) Slip bands in the alloy; (*b*) same as (*a*), but at a higher magnification.   Note the different sets of bands.

contiguous grains of a polycrystalline metal, the so-called grain-boundary effect, is seemingly sufficient to explain what differences in deformation behavior exist between such metals and single crystals.

If a ductile, polycrystalline metal, one whose surfaces have been previously polished and etched, is plastically deformed by a tensile stress; it will be found on microscopical examination that many of the polyhedral grains are crossed by a number of fine, roughly parallel lines—*slip bands*, as they are called (see Fig. 140). These bands are plainly the surface marking of some sort of internal adjusting procedure which the individual grains of the aggregate resort to in order to defer rupture of the metal. From our knowledge of the behavior under stress of zinc single crystals, we may suspect that deformation here has also come about by a series of block slips.[1] The slip bands, then, are irregularities on the metal's polished surface, caused by the projecting ends of the "blocks" that have resulted from the gliding over one another of portions of an individual crystal.

(c) 100 ×.

Fig. 140c.—Cold-worked (compressed) brass, showing distortion of the grains.

This method of deformation in polycrystalline masses is thus nothing more or less than the translation or block slip movement found in the single crystal. In Fig. 139, an attempt is made to picture the gliding supposedly responsible for this method of plastic flow in two contiguous grains. The heavy line is the grain boundary, the dotted lines represent potential slip planes. Since these are certain preferred atomic planes varying in direction from grain to grain, they differ in direction in the two grains shown. After slip has taken place, the reflecting surface of any grain is no longer entirely optically flat, certain portions—specifically, the "exposed" parts of glide planes—are askew. A

[1] According to Zwicky, this "blocking" on deformation is the consequence of an imperfect lattice, that is to say, one in which deviation from strict parallelism in atomic spacing exists throughout the crystal. This is the so-called "secondary" or mosaic structure supposedly found in all crystals. This investigator has designated as π-planes the crystallographic planes which characterize the secondary lattice, and has assumed (it would appear) that gliding occurs on these planes at shearing stresses far lower than those called for by the theory of ideal lattices.

normal incident light beam is reflected from these oblique portions of the surface, not back on itself as occurs elsewhere, but quite outside the microscope's field (Fig. 139*B*).

Application of larger deforming loads increases the number of the slip bands in any one direction in each of the grains involved; also, other sets of bands in a direction different from that of the original set, develop (Fig. 140*b*). Thus we have block slip in more than one direction, and this, if continued to any extent at all, results in actual fragmentation. Distortion of the grains follows, for the grains now change their shape; *e.g.*, they become

Fig. 141.—Cold-worked ferrite grains in commercially pure iron, showing a general elongation of the crystallites in the direction of rolling.   500 ×.   (*Photograph by Reed.*)

generally elongated in the direction of the stress in tensile loading or normal to the direction in compressile loading (Figs. 140*c* and 141). Yet, despite distortion and excessive fracturing of the grains, the boundaries remain remarkably intact.

Briefly, then, the principal visible manifestation of the effects of deformation on a polycrystalline metal are slip banding, grain distortion, and grain fragmentation. All these effects seem not inconsistent with the notion that plastic flow in metal proceeds by block gliding. If our explanation of certain peculiarities in the appearance of X ray diffraction patterns of strain-hardened metal is correct, there are three additional structural effects produced by deformation which are not revealed by simple visual methods. One of these is supposedly caused by the warping of the atomic

planes along which slip occurs, another by the assumption, on the part of the deformed grains, of a preferred orientation, and a third by the presence of internal, localized strains. If an X ray beam of the proper characteristics is allowed to pass through a piece of unstrained, polycrystalline metal foil, behind which is placed at the proper distance a photographic film, the beam becomes diffracted by any and all atomic planes of the metal of the appropriate inclination to the direction of the incident beam. The diffracted radiation, or rather that portion of it which is diffracted into many separate beams, strikes the photographic film, producing thereon a large number of small, distinct, round spots (Fig. 10c). This is the normal "transmission-pin-hole" pattern of a strain-free metal, of rather large average grain size. A similarly made pattern of a strain-hardened metal shows like spots, but these, instead of being truly circular in section, are somewhat distorted, *i.e.*, elongated slightly in a radial direction. The elongation of the reflected spots is explained as due to a slight bending or warping (Biegegleitung) of the gliding planes, a consequence supposedly of the slip movement along them. These planes, as we recall, are the internal "reflection surfaces" of the crystal, and, when perfectly straight, the reflected image of the point source is a true image, *i.e.*, it is circular. When the planes are warped, the image becomes distorted. A likely consequence of plane warping, too, is that slip along such planes is somewhat impeded, since linear translation along bent planes might conceivably occur less easily than along straight even ones. This would appear especially true for those planes which happen to cross other warped ones. Fresh gliding planes could, therefore, be expected to develop whenever slip resistance along old planes becomes greater than that required for the starting of new ones. Indeed, the continual involvement of fresh planes of slip during the progress of deformation seems to be the fact, for microscopical evidence of slip-band formation indicates that slip along any one plane or set of planes does not continue uninterruptedly, but rather that it proceeds to a certain distance, then is definitely checked, with all immediate subsequent deformation of the grains occurring by slip along newly developed planes.

Preferred Orientation.—We have seen that when a single crystal of zinc is stressed in tension, the glide ellipses gradually

rotate in a fashion such that both the ellipsoidal surfaces and the direction of slip along those surfaces tend to become parallel with the axis of maximum stress.   Now a polycrystalline metal's manner of response to a deforming stress is in all essentials similar.   During the cold-working operation, the individual grains of the metal tend also to rotate their planes and directions of easiest slip into favorable positions with respect to the direction of maximum stress, with the same result, though less readily and completely accomplished than was obtained in the case

FIG. 142*a*.—Photogram of cold-drawn molybdenum wire. Broken Debye rings, indicative of preferred orientation.

FIG. 142*b*.—Photogram of cold-rolled aluminum sheet. Broken Debye rings and slight asterism.

of the monocrystalline metal, *viz.*, that the metal plastically deforms without immediate rupture.   The general tendency of the alignment of the preferred slip planes and of the preferred slip directions, in all the grains concerned, results obviously in a gradual changing of a randomly oriented aggregate to one with a distinctly directed orientation.   There is thus produced a definite fiber structure in the cold-worked metal, the degree and character of which depend on the individual metal, on its lattice type, and on the particular method of deformation responsible for it.   One can say, therefore, that cold work, of the proper kind and amount, changes an anisotropic material into a quasi-isotropic one.   The X ray evidence of the directional character, or preferred orientation of severely deformed polycrystalline

metal, is shown in Fig. 142. A very fine grained metal, or what
in effect may be the same thing, a severely fragmented one
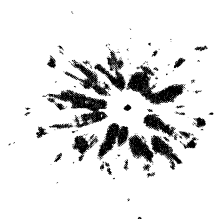
FIG. 143a.—Photogram of cast steel. Few large spots indicate large grain size;
the pronounced asterism reveals the presence of internal strains.
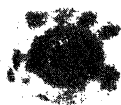
FIG. 143b.—Photogram of cold-worked (rolled) copper, showing some asterism
and the beginning of the formation of the Debye rings.

(that is free from fiber structure), shows a "transmission-pinhole"
pattern consisting of a number of concentric rings. These rings

are due to the reflection from the principal planes of a very large number of small randomly orientated crystals. The rings are continuous, *i.e.*, complete circles of uniform density, if the very small grains (or the granular fragments of a deformed metal) are randomly oriented, but when any amount of preferred orientation accompanies fragmentation, as frequently happens, the rings exhibit areas of varying intensity, even become broken, as shown in Figs 142*a* and 142*b*.

Fig. 144*a*.—Debye ring in back reflection photogram of annealed Armco iron. (*Photograph by Greninger.*)

One further X ray evidence of deformation exists: the broadening of the lines in a Debye pattern. In Fig. 144*a* is given such a pattern for an unstrained specimen of a very pure iron. The lines are sharply defined and rather narrow. A surface working of the iron results in a broadening of the lines (Fig. 144*b*), and since the same amount of radiation is spread over a larger area, the lines become more diffuse. It is to be noted, however, that the distance between the lines (the diameter of the completed circle) remains unchanged, that is to say, that the

Fig. 144*b*.- -The broadened and more diffuse Debye ring of strain-hardened Armco iron. (*Photograph by Greninger.*)

lattice parameter is not altered by strain hardening. The broadening and the greater diffuseness of the spectrum may be ascribed to lattice distortion, perhaps localized, though it may be said that in severely fragmented metal (which the above was not), where the particle size of the crystalline debris is generally smaller than 10^{-4} cm., some of the diffuseness of the lines may be due to the small size of the fragments.

Internal strain is also associated with the presence of radial streaks (asterism) in "transmission-pinhole" patterns of metals which, for any reason, possess residual stresses. Some asterism

is shown in Fig. 143b, which is a photogram of rolled copper, and in Fig. 143a, which is a similar photograph of a cast steel, where internal strains due to nonuniform cooling are present.

In Table 20, are given the principal planes and slip directions of a number of metals and alloys. It will be seen that the favored plane of slip is ordinarily the one of highest atomic density, and that preferred direction of slip along that plane is likewise a thickly populated plane.

TABLE 20.—SLIP PLANE AND DIRECTION OF SLIP IN SOME METALS AND ALLOYS

Metal or alloy	Lattice	Slip plane	Direction of slip	Greatest atom density	
				Plane	Direction
Aluminum.........	Face-centered cubic		[110]	{111}	[110]
Copper............	Face-centered cubic	{111}	[110]	{111}	[110]
Silver.............	Face-centered cubic	{111}	[110]	{111}	[110]
Gold..............	Face-centered cubic	{111}	[110]	{111}	[110]
Copper-zinc (α)....	Face-centered cubic	{111}	[110]	{111}	[110]
Copper-aluminum (α)	Face-centered cubic	{111}	[110]	{111}	[110]
Aluminum-copper (η)	Face-centered cubic	{111}	[110]	{111}	[110]
Gold-silver.........	Face-centered cubic		[110]	{111}	[110]
Iron (α)...........	Body-centered cubic	{110} etc.	[111]	{110}	[111]
Tungsten..........	Body-centered cubic	{110}	[111]	{110}	[111]
Copper-zinc (β)....	Body-centered cubic	{110}	[111]	{110}	[111]
Zinc..............	Hexagonal close-packed	{0001}	[1010]	{0001}	[1010]

Twinning.[1]—So far, we have considered deformation as a simple process of translation, where whole blocks of atoms move

[1] Reference is here made to the formation of twin structures by simple deformation.

en masse, along a gliding plane a certain distance, which is some multiple of the distance between atoms in the direction of shear. In the movement, all atoms involved move the same distance. There is, however, a second way in which a crystal may deform, which, in its mechanism, is perhaps less simple than the one which we have been considering. This alternate way of deforming is known as twinning. In this latter method of a plastic crystal's response to a deforming stress, each plane of atoms concerned moves a certain distance relative to a neigh-
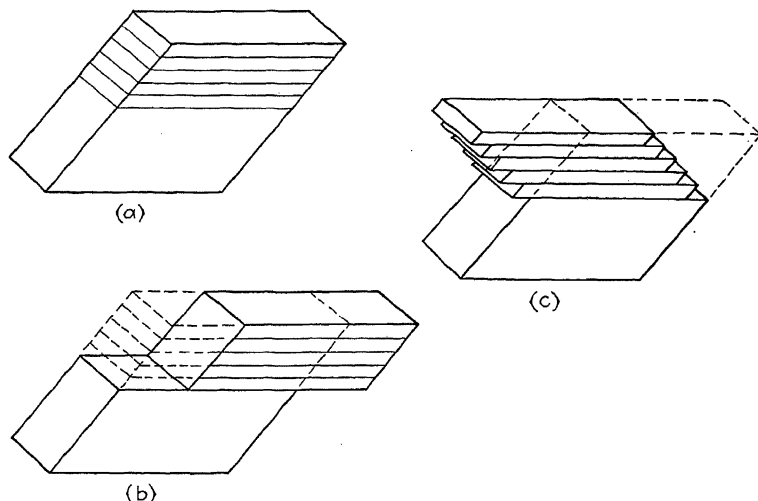
Fig. 145.—Diagrams illustrating the translation and twinning methods of deformation in crystals: (a) crystal before deformation; (b) translation method; (c) twinning (mechanical) method. (*After Schmid and Boas.*)

boring plane, the distance moved commonly being some fraction of the distance between atoms on the twinning plane. To repeat, while in simple translation gliding, all atoms of the "block" move the same distance which is always some multiple of the interatomic distance along the shearing plane, in deformation by twin formation the atoms of a particular plane *only* move the same distance which, however, is less than the full interatomic distance, as measured along the twinning plane. In Figs. 145 and 146 is shown diagrammatically the difference between the two ways in which crystals may deform. In deformation by

slip or simple translation, the two parts of the crystal retain the same general orientation, assuming that no distortion of the lattice or of the gliding plane occurs; in twinning, however, the two parts of the crystal become symmetrical along the twinning plane; each is therefore the mirror image of the other, that is to say, they are twins. The precise reason for twinning under stress is not surely known; in some cases, as in zinc—and perhaps in other metals, too—where the number of available slip planes is severely limited, its purpose seems to be to put

(a)

(b)
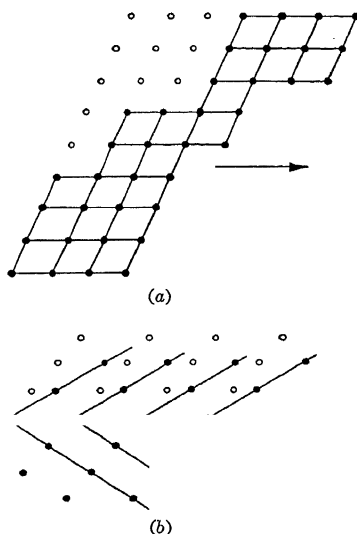
Fig. 146.—(a) Deformation of a cubic lattice by slip (translation). (b) Deformation of a cubic lattice by twinning. (*After Schmid and Boas.*)

those planes into more favorable positions with respect to the direction of stress.

In Fig. 147 are shown mechanical twins (Neumann bands) in alpha iron, and in Fig. 148 are shown what are presumably similar twins in beta brass. Both of these materials, one recalls, are body-centered cubic. In Table 21 are given the twinning characteristics of some of the metals. As in the case of simple-translation gliding, the formation of twins occurs preferentially along certain crystallographic planes.

Property Effects of Deformation.—Quite in line with what one might expect, the metal properties perhaps most affected by deformation are, first, those which offer effective resistance to the deforming stress, and, secondly, those which permit deformation to occur as smoothly as it does. In the first, the deforma-

FIG. 147.—Mechanical twins (Neumann bands) in ferrite. (*Photograph by Reed.*)
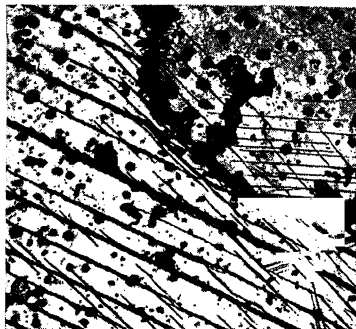
FIG. 148.—Markings in beta brass which may be associated with mechanical twin formation. 100×.

tion-resisting group of properties are the strength and elastic properties: the ultimate strength, the yield strength, the hardness, and the elastic and the proportional limits. These are all increased by cold-working. In the second group of mechanical

TABLE 21.—TWINNING CHARACTERISTICS OF SOME OF THE METALS

Metal	Lattice	Twinning plane	Amount of movement
Iron (alpha)............	Body-centered cubic	{112}	$0.7071a*$
Magnesium.............	Hexagonal close-packed	{1012}	$0.131a$
Zinc..................	Hexagonal close-packed	{1012}	$0.143\dagger$
Tin (white)............	Tetragonal	{331}	$0.120a$

* a = lattice parameter; $0.707 = \frac{1}{2}\sqrt{2}$.

$\dagger\ 0.143 = \dfrac{c/a - 3}{\sqrt{3}}$

properties affected, which one might call the rupture-deferring group, are the plastic and the toughness properties, and these are uniformly lowered by deformation in the cold. It is the latter fact that accounts for the eventual failure of the slip mechanism to function satisfactorily, which circumstance leads inevitably

to the rupture of the metal. But the mechanical properties are not the only ones that are affected by plastic deformation; changes in the physical and chemical properties are also brought about. We shall discuss property changes in that order.

Mechanical Properties.—The effect of varying amounts of cold work on the mechanical properties of brass (67 per cent copper) may be seen in Fig. 118, while the results of a somewhat
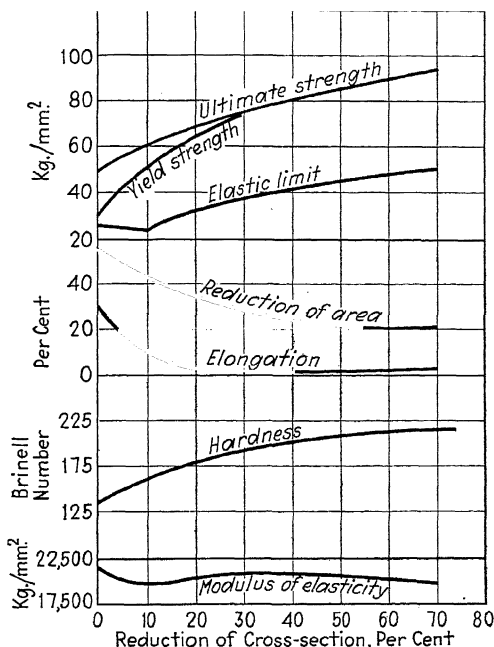
FIG. 149a.—Change of mechanical properties in copper by cold-working (drawing). (*Sachs.*)

more extensive inquiry into the deformation effects on the elastic, strength, and plastic properties of copper and a mild steel are given in Fig. 149. The strength properties, we find, as has already been indicated, are generally raised, while the plastic properties are lowered. The elastic modulus is practically uninfluenced in the case of the steel, and this indifferent behavior seems rather more general than the one of copper which shows a considerable change (a 25 per cent increase). The effects of

deformation on the elastic limit have been summarized by Miss Elam,[1] in part, as follows:

1. The elastic limit in tension or compression is raised by tension or compression toward further stresses acting in the same direction.

2. The elastic limit is lowered by tension toward compressive stresses and vice versa (Bauschinger effect).

3. Metals which are strained beyond the elastic limit and are immediately retested are frequently found to behave as nonelastic bodies, *i.e.*, the stress-strain curve is not a straight line. This property is restored by resting or heat-treatment.
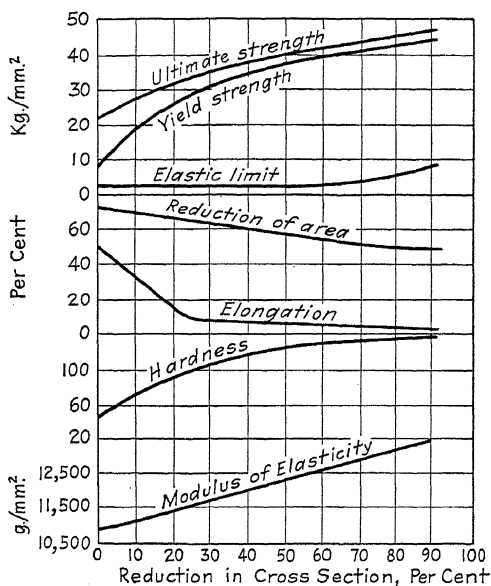
Fig. 149b.—Change of mechanical properties in steel by cold-working (drawing). (*Sachs.*)

Physical Properties.—Various physical properties also undergo change during plastic deformation. The change may be very small and quite inconsequential, as is the case of the density and the thermal expansion, or it may be considerable as it is with the electrical conductivity. An abridged tabulation of physical property changes, as the result of cold-working, after Schmid

[1] Elam, "Distortion of Metal Crystals," Oxford Press, p. 134, 1935.

and Boas, is given in Table 22. One may summarize the results given, as follows:

1. The *density* decreases slightly—a matter of a few tenths of one per cent.
2. The *dilatation* is scarcely affected.
3. The *specific heat* appears little, if any, affected.
4. The *internal energy* is increased.
5. A *thermal e.m.f.* exists between strain-hardened and annealed metal.
6. The *electrical resistance* is considerably increased.
7. The *temperature coefficient of resistance* is decreased.
8. The *thermal conductivity* is decreased.
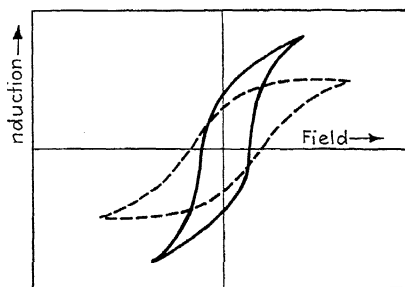
FIG. 150.—Magnetization curves of iron before and after deformation. ———— before, - - - - - after.

In addition to the eight physical effects tabulated, deformation influences also the *magnetic properties* and, in one group of alloys at least, the *color*. The effect of deformation (10 per cent elongation) on the magnetic properties of iron is shown in Fig. 150. There is a general shift in the hysteresis curve toward horizontality, and an increase in the area included within the loop, as a consequence of which there are: (1) a decrease in the saturation value, in the magnetic susceptibility, in the permeability, and in the remanence, and (2) an increase in the coercive force and in the hysteresis loss.

Gold-silver alloys (60 to 70 per cent gold) are white in the annealed condition; on cold-working (rolling), they become first a pale yellow, with a gradual deepening in the color to a deep greenish-yellow as deformation continues.

Chemical (Physicochemical) Properties.—At least two chemical properties—the solution rate and the solution (galvanic) potential—are affected by deformation in the cold. Both

TABLE 22.—CHANGE OF PHYSICAL PROPERTIES BY COLD-WORKING

Property	Metal (or alloy), condition, degree of cold work	Amount and direction of property change

1. Density..............	*Aluminum:* single crystal, elongated 27 %
	Aluminum: single crystal, elongated 40 % (approx)
	Aluminum: polycrystalline, elongated 40 % (approx)
	Iron (Armco); compressed.
	Steel compressed.
	Iron (Armco); rolled 70 %
	Iron (Armco); drawn 4 %
	Steel: drawn 5 %
	Copper: hammered 60 %
	Copper: drawn 60 %
	Copper: elongated 4 %
	Bismuth: extruded wire
	Brass (alpha) 91 % Cu
	  single crystal, extended 70 %
	  polycrystalline, extended 70 %
	Brass (alpha) 85 % Cu
	Brass (alpha) 63 % Cu
	  single crystal
		0
		Change within experimental error (±.02 %)
		
		−0.3 %
		−0.1 %
		−0.1 %
		−0.12 %
		−0.36 %
		−0.51 %
		−0.2 %
		−0.3 %
		−0.13 %
		Slight reduction
		
		+0.13 %
		No definite change
		0
		
		−0.16 %

2. Thermal expansion....	*Iron* (ingot iron), rolled 50 % *Bronze* 50 %	±0.1 % ±0.10 %
3. Specific heat.........	*Iron* (ingot iron): 90 % reduction *Iron* (Armco) and mild steel: hammered *Nickel:* drawn 99.5 % *Tungsten:* drawn 94 % *Bronze:* up to 90 % reduction	~0 +3 % Change within experimental error (±0.5 %) Change within experimental error (±0.5 %) ~0
4. Internal energy........	*Aluminum:* single crystal, approx. 55 % elongation *Aluminum:* polycrystalline, approx. 20 % elongation *Copper:* polycrystalline, approx. 20 % elongation	~0.11 cal./gm. ~0.10 cal./gm. ~0.07 cal./gm.
5. Thermal e.m.f. (with similar annealed material)	*Aluminum:* drawn and rolled *Nickel:* drawn and rolled *Copper:* drawn and rolled *Silver:* drawn and rolled *Gold:* drawn and rolled	+20 to +60 × 10⁻⁸ V/°C.
6. Heat conductivity.....	*Copper:* single crystal, hammered	−73 %

7. Electrical conductivity.	*Iron:* (Armco): drawn 4 %
	Steel: drawn about 90 %
	Steel (1.3 % C): extended 4.5 %
	Nickel: drawn 99 %
	Copper:
	  Drawn 82 %
	  Drawn 40 — 80 %
	  Drawn 4 %
	Molybdenum: drawn 99 %
	Silver: drawn 60 %
	Tungsten: drawn 99 %
	Platinum: drawn 99 %
	Brass:
	  α-brass, drawn 4.3 %
	  α and β, drawn 4 %
		+ 0.96 %
		+ 2 %
		+ 0.29 %
		+ 8 %
		
		+ 2 %
		+ 2 %
		+ 1.5 %
		+18 %
		+ 3 %
		+50 %
		+ 6 %
		
		+ 1.6 %
		+ 1.0 %

8. Temperature coefficient of resistance	*Nickel:* *Molybdenum:* *Tungsten:* *Platinum:*	− 5 % −16 % Drawn 99 % −35 % − 7 %

* After Schmid and Boas (abridged), from their "Kristallplastizität," (1934).

effects are technically important since they play an important role in corrosion and allied phenomena (season cracking, corrosion fatigue, etc.). The rate of solution of worked metal is higher than that of the annealed condition, the actual rate of the former varying, though possibly nonuniformly, with the amount of cold work (see Fig. 151). If two metals, one strain-hardened and the other strain-free, are placed in an aqueous solution of one of the metal's salts (thus forming a galvanic cell), it will be found that the worked metal becomes electronegative to the nondeformed one. The difference in solution potential

Fɪɢ. 151.—Curve showing the effect of the amount of cold-working (extension) on the solution rate of steel in acid.

between work-hardened and annealed metal in the same sheet or plate may be responsible for instigating and accelerating corrosion of the sheet or plate.

Causes of Property Changes in Cold-worked Metal.—The changes in properties on cold-working can more readily be appreciated and evaluated, and the precise mechanism can more easily be discerned, than can reasons be given why the ascribed manner of plastic flow should produce the effects that it does. Naturally, such an intriguing matter has occasioned a great deal of speculation. In general, one of three principal reasons has been given by any who have ventured an explanatory hypothesis for cold-working effects on properties: first, that deformation produces a definite change in phase, and that the mere presence of this new phase in appreciable amounts is responsible for the change in properties; second, that the observed changes in structure (fragmentation, directed orientation, etc.) are in themselves sufficient, by reason of purely mechanical effects—and quite apart from any possible change in state—to produce the property changes; and third, that deformation produces internal strains within, and increases the internal energy of a metal, and that these circumstances explain the peculiar properties of a cold-worked metal. Objections, of one sort or another, can be raised to any one of the three explanatory hypotheses. It is a fact that no one explains satisfactorily all the observed effects and phenomena of strain hardening, and in view of the

number and diversity of these effects and phenomena, it seems unlikely that any notion can, at once, be sufficiently comprehensive and really simple.

The Amorphous-metal Hypothesis.—This ingenious theory, proposed by Beilby, is an extension of the amorphous-surface-film concept (Beilby's also) to the gliding surfaces concerned in slip within crystals. Beilby's original notion was that amorphous, *i.e.*, isotropic metal forms on highly polished metal surfaces, essentially in this way: the pressure applied in burnishing momentarily "melts" a very thin layer of surface metal; this liquid film is, at the instant of its formation, extremely tenuous and mobile, and as a consequence readily flows under pressure, forming an overlay on the surface. But, then, almost immediately, the liquid congeals, without actually crystallizing, into a blanketing film of rigid, amorphous metal.

Furthermore, Beilby would not limit amorphous film formation to the external surfaces of polished metal, but would picture an analogous series of events as taking place during plastic deformation along the planes actually involved in slip. Then and there, by reason of the pressure exerted by the deforming stresses, a quite superficial melting of the metal on the gliding planes occurs, the liquidity of the film produced, for the moment, accelerates slippage, but congelation almost instantly sets in. Then, the solid, amorphous cement inhibits further slip along that particular plane, forcing it to occur, if deformation is to continue, along fresh planes. Moreover, the formation of an intracrystalline, isotropic phase changes an hitherto wholly crystalline metal into a partly amorphous one.

Amorphous metal, in common with other undercooled liquids, like glass, has certain specific properties. It is hard, yet less dense than the same material in a crystallized form. It is brittle to stresses that are suddenly applied, yet yields gradually (creeps) if application is slow. It is less conducting, more elastic (being a liquid), and possesses higher vapor and solution pressures than the corresponding crystalline form. Furthermore, on heating, amorphous metal crystallizes (devitrifies). It is this hard, strong, and less dense amorphous phase on the interfaces of the displaced portions of the strain-hardened crystal(s) which, according to Beilby's notion, accounts for the characteristic properties of cold-worked metal.

The theory explains rather satisfactorily many of the property changes associated with the cold-working process, such as, for example, the changes in the mechanical properties, in the density, in the electrical conductivity, and in the urge of strain-hardened metal to recrystallize on heating. Objections to the adequacy or even to the fundamental soundness of the theory have been raised principally because X ray studies of strain-hardened metal, on the one hand, fail to detect isotropic metal either on polished surfaces or along glide planes and, on the other hand, show—according to some—definite evidences of quite another cause, *viz.*, the existence of internal strains. It is also found that strain-hardening is rather general throughout a wrought metal, *i.e.*, the hardness increase is not confined to the slip planes or to the regions immediately adjacent thereto. This recent discovery is offered as further proof of the incorrectness of the theory. It should perhaps be noted, however, that, as far as X ray diffraction methods are concerned, their failure to find amorphous metal either within or without a crystal is not necessarily conclusive evidence that such metal does not exist; it may only mean that these methods are insensitive under the prevailing conditions. As a matter of interest, it has recently been shown[1] that quasi-isotropic metal does, in fact, exist, at least, on polished metal surfaces.

Structure, Strain and Energy Effects as Causes of Property Changes.—Because of the interrelation of many of these effects of deformation as possible causes of property change, one may well consider them together. The gross and fine structure effects of cold work are varied: fragmentation of the individual crystallites due to polydirectional block slip; a definite departure of these same crystallites from an equi-axed condition; a directed orientation of the crystallites, the result, as has been explained, of the latter's attempt to align its preferred slip planes and slip directions in a definite relationship with the direction of maximum stress; a warping, or even a buckling of the gliding planes; and, finally, a distortion of the lattice which, supposedly, is the source of the residual strains in the metal. One has thus quite an assortment of rather fundamental phenomena which one may utilize to develop an explanatory theory. As one might expect,

[1] Finch, *Proc. Roy. Soc.*, **5**, 145A (1934); also Rupp, *Kolloid-Zeitsch.* **69** (1934).

the opportunity presented has not gone a-begging.   There have been suggested a large number of hypotheses, some more convincing than others, and no one really satisfying.   But no attempt will be made here to review them.[1]   It may be said, however, that generally some properties of cold-worked metal are more easily and satisfactorily explained by one effect than are others.   For example, the mechanical properties are perhaps most simply accounted for by the fact of fragmentation, for granular fragments conceivably act in much the same fashion and presumably with equal effectiveness as do whole grains in increasing resistance to slip.   On the other hand, a directed orientation is an unlikely cause of strain-hardening effects since it can be easily shown that the effects precede by some time the first evidences of a preferred arrangement.   Yet neither fragmentation nor an orientation change is a simple answer to the observed lowering of the density.   This particular property change, especially because the change is in the direction that it is, suggests quite another cause, *viz.*, the formation of an amorphous phase.   The matter of the effect of the buckling of the glide planes during slip on strengthening the lattice has already been alluded to.   Again, others would ascribe the circumstances of lattice distortion and internal strains as basically the agencies at work in producing strain-hardening.   They are of some influence, certainly; the change in certain mechanical properties, the increase in electrical and thermal conductivities, and the increase in chemical activity might conceivably be explained on these grounds.

One might point out the general similarities of effects of alloying and cold-working.   Both procedures increase the strength properties, the resistance to further deformation, and the electrical and thermal resistances.   Cold-working increases the solution potential and the susceptibility to corrosive attack; alloying usually does also, though as we know, there are a few well-known exceptions.   The plastic properties are commonly lowered by alloying, invariably so by deformation.   There is, however, one distinct difference in certain X ray diffraction effects produced by the two processes: deformation produces a diffuseness of the Debye rings but does not change their diameter,

[1] An excellent summary may be found in the closing chapters of Miss Elam's book, "Distortion of Metal Crystals."

while alloying (the solid solution) shows the opposite effect in that the rings remain sharply defined but their diameters are changed.

The whole phenomenon of plastic deformation, but more particularly the possible reasons why the physical properties change as they do, is still largely an enigma. There are some indications that the problem may resolve eventually into one for the atomic physicist. At least Tammann thinks so, and Miss Elam, in a concluding paragraph of her recent book, writes of a similar conviction.[1]

FIG. 152a.—0.30 per cent carbon steel, as cast. Coarse structure. 100 ×. (*Photograph by Reed.*)
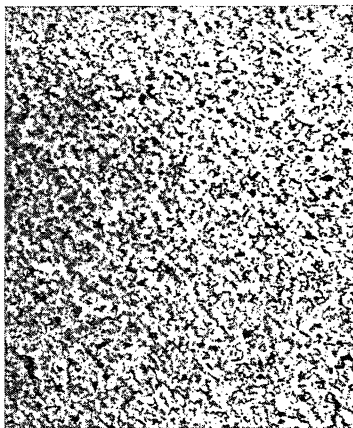
FIG. 152b.—0.30 per cent carbon steel, hot rolled. Fine structure. 100×. (*Photograph by Reed.*)

Hot Working.—In general, working below the recrystallization temperature of a metal constitutes cold-working. Hot working obviously then means deforming above that temperature. The case of steels of moderate or high-carbon content is a special case since the predominant microconstituent of these steels (pearlite) does not readily recrystallize until it can do so as new austenitic grains, which is some 300°C. above the temperature where severely deformed iron will recrystallize.

[1] " . . . as the problem of plastic deformation is part of the more general one of cohesion, it seems likely that the structures of atoms and the action of interatomic forces will ultimately provide the true explanation."

Hot-working methods are of various kinds—rolling, forging, extruding, pressing, etc. Metallographically, these methods are important because of their general refining and homogeneizing effects on coarsely dendritic and eutectic structures. These generally undesirable structures are broken up by the hot-working procedures, and the constituents refined and distributed uniformly. In Fig. 152 are shown the effects of hot rolling on the microstructure of a 0.30 per cent carbon steel; and in Fig. 153 similar refining and redistribution effects in a steel of hyper-

FIG. 153a.—1.25 per cent carbon steel, as cast. Pearlite and pro-eutectoid cementite in grain boundaries. 500×. (*Photograph by Reed.*)
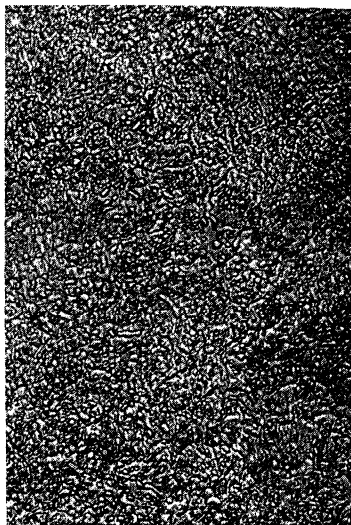
FIG. 153b.—1.25 per cent carbon steel, hot rolled. Fine cementic structure. 500×. (*Photograph by Reed.*)

eutectoid composition. Figure 154 illustrates the breaking up, by forging, of the coarse eutectic in a high-speed steel.

The hot working of a definitely dendritic structure often results in the reshaping of the dendritically segregated areas; in the case of rolling, they are strung out in the direction of rolling. The banded structure in the carbon steel of Fig. 155 came about in that manner. The sinuous "flow lines" in the deeply etched, forged gear (Fig. 156) result from superimposing upon the rolled stock the forging operation used to produce the teeth of the gear.

Thermal or Heat-treatment.—The properties of many alloys are not wholly independent of the circumstances of their genesis

and history. Some alloys are especially sensitive to the conditions of their immediate past; their properties are largely conditioned on what, in the way of temperatures of heating and rates of cooling, has gone on before. This is due to two facts: first, and fundamentally, to the fact that phase and other structure-determining changes take place in these alloys; and, second, to the fortunate circumstance that the changes, or at least certain phases of them, occur slowly, even leisurely. Thus, past conditions of temperature and time—the time at a particular temperature or temperatures, and the time given for cooling from the temperatures—determine, in no small measure what the general or specific properties of the alloy shall be.

FIG. 154a.—High-speed steel, as cast. Coarse dendritic structure with eutectic fillings. 500 ×. (*Photograph by Reed.*)

The second of the facts mentioned, the general sluggish character of the changes occurring, is of practical significance, for it is the time-consuming nature of these changes which places them (and indirectly the properties which originate from them) under man's purposeful control.

The methods of intentional regulation and control of an alloy's properties are called collectively *heat- or thermal treatment.* The different procedures used that fall under that category—and there are many of such—may be much alike in intent, but they vary a great deal in method; yet all invoke the use of high temperatures and exercise control, at one or another stage of the process, of the time element. Also, the actual procedures differ widely in their action and consequences, depending as these do on the nature and the kinetics of the alloy's structural change which they would control and regulate. In some instances, heat-treatment is simply modifying in its effects;

that is to say, certain existing properties of the untreated alloy are materially improved by the treating process and the alloy becomes thereby a better and a definitely more useful alloy, generally or particularly.   This is true of most age-hardenable alloys, a kind of heat-treatable alloy which we shall have occasion to describe later on.   On the other hand, heat-treatment may be more decisive and thoroughgoing in its workings and in its effects; then actually new, commonly specific, properties may
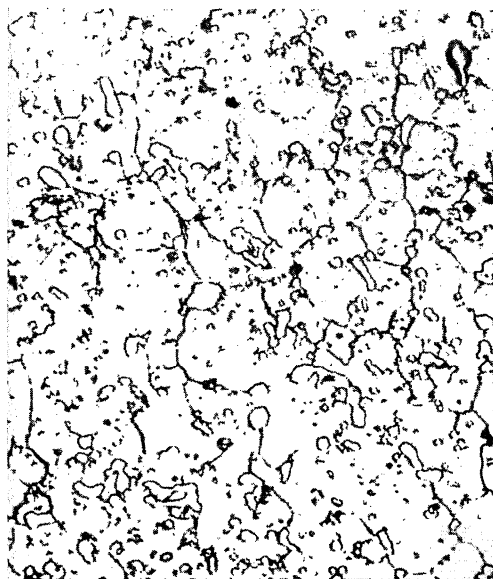
FIG. 154b.—High-speed steel, forged and heat-treated.   Small spheroids of carbide in an austeno-martensitic matrix.   1000×.   (*Photograph by Reed.*)

be created or original general ones so changed that one may find little quantitative resemblance between the old order and the new.   Examples of these more fundamental and sweeping changes in an alloy's properties by heat-treatment are afforded in the heat-treatment of steel, a matter which again will claim our attention later.   Again, in other cases, as in the annealing of strain-hardened metal, heat-treatment is merely remedial or corrective in purpose—to remove undesirable properties which have been acquired in processing.   Heat-treatment, in this sense, becomes a normalizing procedure.

In most of the structural changes in alloys which result in property betterment and which are controllable by heat-treat-

Fig. 155.—Banded structure in a 0.50 per cent carbon steel. 100 ×. (*Photograph by Reed.*)
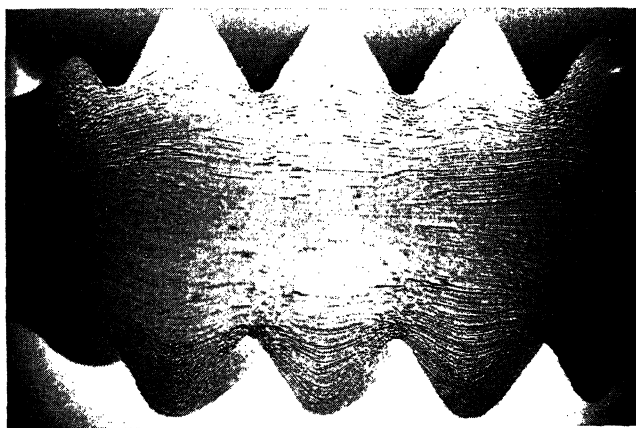
Fig. 156.—Macrograph of a forged gear, showing the "flow" lines developed by deep etching.

ment, recrystallization phenomena, in one form or another, are implicated. It may be that the consequence of the recrystal-

lization process is simply a new set of crystals whose individual units are, in matters of composition and crystallographic character, identical with the parent crystals. This is precisely what happens when strain-hardened metal is annealed. Then, the internally strained, distorted, and even fragmented grains recrystallize when heated to the proper temperature, a new set of grains forms *in situ*, but the latter, while quite strain-free, whole, and equi-axed, are nevertheless chemically and crystallographically like the old crystals. But on occasion, recrystallization is a more subversive phenomenon; then an exhaustive reorganization of the crystalline structure results and one secures a new set of crystals and a set of new crystals as well. The eutectoid inversion represents such a thoroughgoing type of recrystallization. On slow cooling through the critical temperature, the inversion of the parent phase, a solid solution results in the simultaneous recrystallization of two altogether new and distinct crystalline species. The derived phases necessarily differ from one another chemically; neither is like the parent. In the matter of lattice, the new species may differ between themselves, and yet neither be fine-structurally like the common parent.

The precipitation of the excess solute from a supersaturated solid solution is an example of recrystallization where the derived phase is chemically and (usually) crystallographically unlike the original solution. A case where the precipitating phase is an intermetallic compound will serve as an illustration, *e.g.*, the age-hardenable aluminum copper alloys. An example of crystallographic similarity between the parent and the derived phases of such a system is found, however, in the copper-silver system, where a heating of either of the rapidly cooled, supersaturated, terminal solid solutions results in the precipitation of the corresponding conjugate solution of a different chemical composition necessarily but of the same lattice type (see page 143).

The gold-copper system provides a further variation of the consequences of recrystallization. It is now generally considered proved that the stable phase, below about 420°C., in the alloy of equi-atomic ratio is tetragonal. The alloy structure above this temperature is cubic. We have thus a change on cooling, and on heating, in this temperature vicinity in

which a change in lattice occurs with no change in chemical composition.

The properties peculiar to a heat-treated alloy may not, however, be entirely determined by the nature or the extent of the recrystallization change. Frequently, in a not inconsiderable measure, these properties are influenced by the dimension of the recrystallized grains or particles and by the manner of their distribution in the residual parent matrix. These matters are of some consequence in age-hardenable alloys; moreover, in certain of these alloys it would appear that actual recrystallization is not a prerequisite for property modification. The fact of the imminency of the phenomenon seems sufficient.

Before we consider, as we shall do, some representative heat-treating procedures, we might, by way of introduction, briefly describe an illustrative example of a heat-treatable alloy system. The phenomena met with in this system are rather fundamental and fairly typical of the more technically important cases to be discussed later. The example is now given, with only enough explanatory comment to make it meaningful. Interpretive details of the mechanism and kinetics of the phenomena implicated are given somewhat farther along in another connection.

The Gold-copper System.—This system, already cited as one illustration of what may happen when recrystallization occurs, freezes in what essentially is a continuous series of solid solutions, though there is a minimum on the freezing-point curve (see Fig. 157). Both metals are face-centered cubic, and the solid solutions that result from primary crystallization are of this type. The two metals are randomly distributed at first in the solid-solution lattice. On cooling to room temperatures, however, the alloys, or more exactly those of certain compositions, experience changes in their fine structure. The equi-atomic composition (AuCu), and the compositions given by the formulas (AuCu$_3$) and (Au$_2$Cu$_3$) are the ones affected. These compositions are indicated by the three maxima of the major curve in the equilibrium diagram. The change on slow cooling occurring in the alloys in the vicinity of the composition (AuCu$_3$) is definitely associated with the formation of a superlattice. Above 400°C., the copper and gold atoms are arranged in the face-centered cubic solution quite by chance; below there is a disposition on the part of each species to take up definite positions relative to one

another, *i.e.*, below 400°C. the alloy becomes a symmetrical solid solution.   Moreover, this change in fine structure is a reversible one, and the symmetrical solution passes without marked hysteresis effects on reheating through 400°C. into a solution where random placement again prevails.   The change from a random to an ordered arrangement is not brought about instantaneously; but like most structure changes in which atomic migration is involved, the element of time enters.   A complete transformation from one condition to the other requires, in fact,
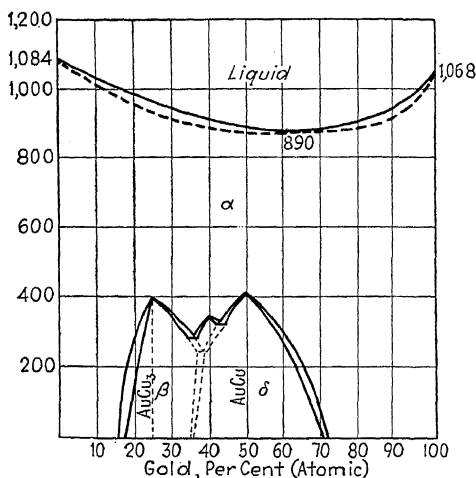
Fig. 157.—Gold-copper equilibrium diagram.   (*After Houghton and Payne, and Kurnakow.*)

a very slow rate of cooling through the transformation temperature; if the rate of cooling be accelerated, the change will be more or less incomplete, while a definitely rapid rate of cooling, as would follow from a water quench, would prevent the change altogether.

   The properties of the solution with the constituent atoms distributed randomly on the lattice differ decidedly from those of the solution where an ordered lattice arrangement exists; in other words, the properties of this alloy at room temperatures are in no small part determined by the rate at which the alloy cools to these temperatures.

This same sort of qualification, but with even greater truth, applies to the properties of the alloy of this series of equi-atomic composition. This, too, is a composition at which a pronounced maximum on the major curve exists (see Fig. 157). The transformation here at about 420°C. is indeed a real change in lattice configuration, not simply a rearrangement within a lattice type as in the previous composition. The face-centered cubic gold-copper lattice, stable at high temperatures, changes at about 420°C. to a tetragonal one. It is a reversible one on heating, and one which exhibits a definite hysteresis. Here again, the time given for the change to occur determines the completeness
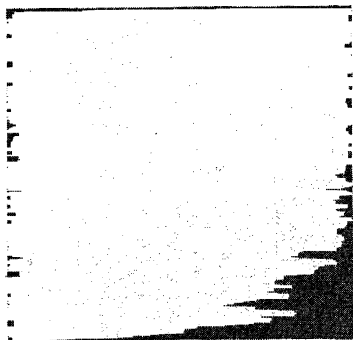
FIG. 158a.—Fifty per cent gold-copper alloy. Quenched from 650°C. 100 ×. (*Photograph by Peterson.*)
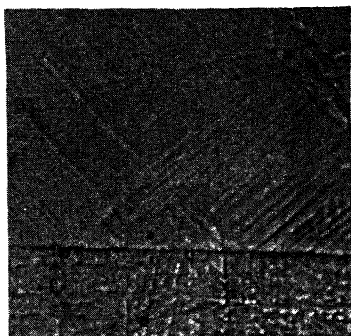
FIG. 158b.—Fifty per cent gold-copper alloy. Quenched as in Fig. 158a, and then reheated to 300°C. for ½ hr. 100 ×. (*Photograph by Peterson.*)

of the change—both on heating and on cooling. A rapid enough cooling through 420°C. prevents the change from occurring at all; then, the high-temperature condition of the alloy, the face-centered cubic configuration, survives the drastic quench and becomes the crystallographic form of the alloy at room temperatures. Of course, this solution is structurally unstable. In Fig. 158a, is a photomicrograph of a quenched alloy of this composition.

Again, the properties of the rapidly cooled alloy differ from those of the slowly cooled. Comparative mechanical property curves of the quenched and the slowly cooled alloys of the complete gold-copper series are shown in Fig. 159. One notes that the slowly cooled, supposedly structurally stable alloys, in

particular the one of AuCu composition, have generally higher strength, and lower plastic property values than do the quenched alloys. How much of this increase in the one case and decrease in the other is actually due to the presence of the tetragonal phase (in the case of this particular composition), and how much is due to the *way* this phase is present, is not certain. That distribution is of some significance will be evident from the paragraphs that follow. But we have here, in externals at least, a simple enough case where a difference in heat-treatment—specifically a variation in the rate of cooling through a critical temperature—produces a change in properties in an alloy. The example typifies a case of *suppressed transformation.*

The quenched AuCu alloy is amenable to further heat-treatment. Because the alloy is structurally unstable, if given the opportunity, its cubic phase will slowly revert to the stable tetragonal one. This chance is given if the alloy is heated for a sufficient length of time to some temperature below the transformation temperature of 420°C.

After quenching
After slow cooling
(After Broniewski and Wesolowski)

Fig. 159.—Mechanical properties of the copper-gold alloys.

The change in fine structure is accompanied by a slight change in the micro-appearance of the alloy (see Fig. 158b), and by a definite change in certain properties. The change in the hardness, for example, brought about by reheating the quenched alloy for different time periods, to 100, 150, 200, 300, and 400°C. (all these temperatures being below

the critical temperature, though the last is scarcely below)
is shown in Table 23. The Rockwell *B* hardness of the quenched
alloy is 71.5. On reheating this alloy at 100°C., for time periods
ranging from 15 min. to 200 hr., the samples show a consistent
increase in hardness to a maximum of 91 for the sample annealed
for the 200-hr. period. Since the hardness is still increasing at
200 hr., a longer heating period would evidently increase the
hardness beyond 91. It is the same story for the 150° and the
200°C. anneals. Only in either of these two cases the hardness

TABLE 23.*—AGE-HARDENING OF THE WATER-QUENCHED (650°C.)
Au-Cu ALLOY

Time of anneal, hr.	Rockwell *B* hardness				
	100°C.	150°C.	200°C.	300°C.	400°C.
As quenched	71.5				
0.25	77.0	84.0	101.0	102.0	87.0
0.50	80.5	89.0	102.5	103.5	85.0
1.00	82.5	91.0	103.5	103.5	83.0
2.00	83.5	92.0	104.5	104.0	81.0
4.00	84.0	94.0	104.7	104.0	81.0
20.0	85.0	95.0	105.0	103.6	80.7
100.00	87.5	96.0	105.2	99.5	
200.00	91.0	99.0	105.5	95.0	80.0

* From the results of Dr. A. W. Peterson (Thesis: "Transformations of Gold-copper and Gold-copper-zinc Alloys," Harvard Graduate School of Engineering, 1934.

of the sample for any time period is always higher than in the
former case; also, the hardness of the alloys reheated to 200°C.
for any particular time period is always above that of the alloy
heated to 150°C. for the same period. The hardness (about 105)
found and consistently maintained from 4 hr. onward in the
200°C. series is apparently the maximum hardness obtainable
in this or in any other of the series. The series reheated to a
temperature of 300°C. behave somewhat differently from any
of the foregoing. In the first place, the initial rise in hardness
is very rapid—the maximum hardness is obtained in 2 hr. and
almost so in 15 min.; furthermore, a definite softening takes
place in the alloys beginning with the 100-hr. specimen. The
alloys annealed at 400°C. never develop the maximum hardness
found in the other alloys, or perhaps more correctly the maximum

hardness came early in the 15-min. interval and thus escaped detection. Softening is marked after the low maximum on the longer heating periods.

We, of course, understand that the property changes incurred in the annealing of the quenched gold-copper alloy are in some way associated with the gradual decomposition of the unstable cubic solid solution and the formation in its stead of the stable tetragonal one. But still these changes cannot be all due to the simple replacement of one kind of solution by another, for, if this were all there was to it, the conditions most favorable for a complete transformation, *i.e.*, a long time or a high temperature of anneal, would result in the greatest change in hardness. This is exactly what does not happen, for there is, as we have seen, a distinct softening below the maximum value when either the time at a particular temperature is unduly increased, or when for a given interval the annealing temperature is unreasonably high.

It has been proposed that in the so-called age-hardening alloys, of which this alloy is one example, the increased resistance to slip which results, for one thing, in greater hardness, is due to the form and position assumed by the phase precipitated as a result of the breakdown of the unstable solution. According to this notion, the particles of the new phase that happen to form along potential slip planes become the active ones in impeding slip, and when the number and size of such particles are just right, *i.e.*, critical, their action is really very effective. A hypocritical dispersion, the condition prevailing during the initial moments of anneal, particularly at the lower temperatures, is less effective, while a condition of hypercriticalness—a small number of rather large particles—likewise results in comparative impotency. Excessive particle growth at high temperatures, or at lower ones if sufficient time is given, is the assumed cause of the softening of the alloy which eventually occurs.

Annealing.—This term was used in the foregoing discussion of the heat-treatment of the gold-copper alloy when one had occasion to speak of the reheating of the quenched alloy. The word itself is an old one, and in the older, historic meaning, it indicates a heating operation followed by a gradual cooling. This is the sense in which it is still used in the heat-treatment of steel. But with the advent of the heat-treatable, *i.e.*, age-hardenable,

nonferrous alloys, the qualifying phrase describing the manner of subsequent cooling came to be disregarded, until now almost any heating operation regardless of the rate or manner of the cooling process which immediately succeeds the application of high temperatures has come to be designated as an annealing operation. We shall find, therefore, that contemporary usage of the term is not always consistent, at least insofar as the cooling-rate phase of the operation is concerned. But the term invariably refers to a high-temperature heating operation and is now often preceded by a descriptive adjective to indicate the precise objective of the operation. We shall next review briefly some representative annealing operations, starting with the two that have been described as corrective in purpose.

Homogeneizing Anneal.—Because of the fundamental selective nature of the freezing procedure of solid solutions, and because diffusion ordinarily does not keep pace with crystallization during solidification, cast solid-solution alloys are more or less chemically heterogeneous. Thus, as we have seen, is the origin of the form of segregation found in such alloys known as dendritic segregation. It is obviously an unstable condition, yet often one that is peculiarly persistent. But, by suitable heat-treatment, or more quickly and thoroughly by a proper combination of mechanical and heat-treatments, dendritically segregated alloys can be homogeneized and granulated, and their heterogeneous macrodendrites replaced by chemically uniform micrograins. Several microstructures of cast alloys have already been given in Chap. V; another such structure, that of a 1 per cent silver, copper-silver alloy, is shown in Fig. 160*a*. The axes of the dendrites in this alloy are the copper-rich solution. The fillings are relatively rich in silver. There is a definite localized difference in composition throughout a given dendritic area. The homogeneized microstructure of the same alloy (Fig. 160*b*) shows this difference removed. In the latter alloy, granulation—a resizing and reorienting form of crystallographic reorganization—has replaced the large, indefinite dendritic masses with small distinctly polyhedral grains; at the same time, diffusion has been briskly active, atoms of silver and copper have moved countercurrently from localized high concentration areas to lower ones, resulting in a general chemical uniformity throughout each grain and throughout the aggregate.

A photomicrograph of a bronze in the process of granulating and where homogeneization is only partly complete is shown in Fig. 161. (Compare this photograph with Fig. 62 of a cast bronze that has had no treatment at all; the general diffuseness of the dendritic pattern of the partly homogeneized bronze becomes then the more evident.)

Temperature and time are the two external factors principally involved in the homogeneizing anneal. The higher the temperature, the shorter will be the time necessary. Diffusion rates are dependent upon temperature, but at any temperature these are determined by the relative size of the migrating atoms, by the

Fig. 160a.—Copper-silver alloy (1 per cent silver). As cast. Dendritic structure. 100 ✕.

Fig. 160b.—Same alloy after homogeneization treatment (annealing). Polyhedral structure. 100 ✕.

lattice type of the solution, by the degree of solid solubility, etc. The accelerating effect of working on diffusion and homogeneization when such material is subsequently annealed is assumably due to the "looseness" of a strained lattice, facilitating readjustments which depend upon atomic movement.

Annealing of Strain-hardened Metal.—Of the peculiar properties of cold-worked metal, none is perhaps more important technically than the ability to recrystallize, to form, of itself, if conditions permit, a new crystalline conglomerate whose several grains are, as has been stated, strain-free, whole, and equi-axed. That is, there is no more important property than this, save that these recrystallized grains are capable of growth to dimensions which are determined, on the one hand, by the

degree of previous deformation, and, on the other, by the temperature and time of the annealing operation itself. Recrystallization and grain growth are physically indistinguishable, though complementary phases of a single phenomenon; no sensible boundary, in any physical sense, differentiates them as far as anyone can tell. Yet for purposes of study it may be convenient to discuss certain aspects of each separately.

When a metal is heated, it will recrystallize, provided (1) that the metal has been previously strained (not necessarily cold-worked, though this is usually the most effective way of strain creation), (2) that the temperature is sufficiently high, and (3) that the time of heating is sufficiently long. The particular temperature at which incipient recrystallization

Fig. 161.—Partly homogeneized and granulated structure in a copper-tin alloy.

occurs depends upon the amount of deformation. The greater this is, the lower will be the recrystallization temperature. This is as one might expect, since the greater the degree of the instability or strain present, the greater is the urge of the metal to regain normalcy, and the sooner, in point of time or temperature, will it respond to a normalizing environment. The minimum temperature required for the recrystallization of worked metal, that is to say, the recrystallization temperature of severely worked metal, has been determined in a few cases only. The observations (given in Table 24) are, as one must know, only approximate. In Table 24, the last column gives the ratios of the melting temperatures and the recrystallization temperatures (both in degrees absolute). The circumstance that

these temperature ratios are fairly constant is interesting, perhaps significant.

TABLE 24.—APPROXIMATE RECRYSTALLIZATION TEMPERATURES OF SOME SEVERELY DEFORMED METALS

Metal	Approx. recrystalliza-tion temperature, °C.	$T_{\text{melt.}}/T_{\text{recry.}}$
Molybdenum	900	2.4
Zinc	Room temperatures	2.3
Iron	450	2.5
Nickel	600	1.98
Gold	200	3.00
Silver	200	2.6
Aluminum	150	2.2
Magnesium	150	2.1
Tungsten	1200	2.4

The velocity of recrystallization on heating a strain-hardened metal depends on both the temperature (assuming, of course, this is high enough to cause recrystallization at all) and on the degree of previous deformation. The relationships are shown
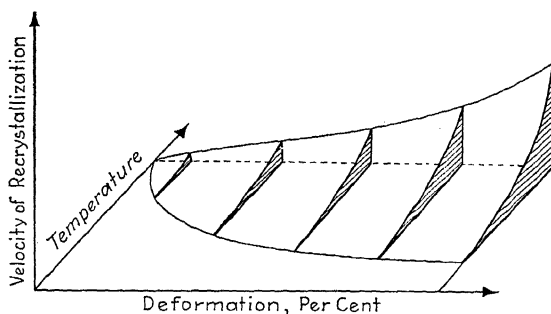
FIG. 162.—Diagram illustrating the relation between the velocity of recrystallization, the temperature, and the amount of previous deformation. (*After Czochralski.*)

in the diagram of Fig. 162. Recrystallization, as we see, occurs most rapidly at higher temperatures and with greatest amounts of deformation.

The structural reorganization brought about by recrystallization results, as has been stated, in the formation of a new set

of small, strain-free crystals, which are now capable of growth.
The want of any strain whatsoever and the ability to grow in any
degree seem inconsistent, for, unless our present notions are in
error, a strainless grain is dimensionally stable. As a matter
of probable fact, the fledgeling crystallites are not absolutely
free from strain; they are only freer from strain—manifestly,
much freer—than were their predecessors. There is some
evidence that warrants one in believing that this is so, *e.g.*,
the etching characteristics of partly recrystallized metal. Simi-
larly, distortion and directed orientation effects of deformed
metal are often persistent, and slight evidences of either may
survive what is otherwise an adequate annealing treatment.
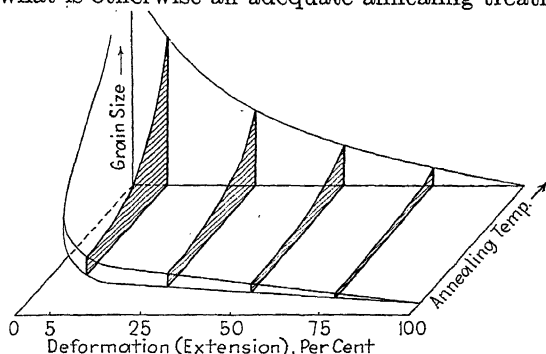
FIG. 163.—Recrystallization (grain-growth) diagram of a metal. (*After Czochralski.*)

So, supposedly because of small residuary strains, the small
crystallites of recrystallized metal grow, on further annealing,
at such a rate and to that size which temperature, time, and the
degree of original strain permit. The final grain size is thus
determined by at least these three factors. Grain-size depend-
ence on the temperature of the anneal and on the degree of
deformation—two interdependently controlling factors, by the
way—is shown diagrammatically in Fig. 163. One finds (1)
that a certain annealing temperature (for the time given) must
be attained before any significant amount of grain growth
occurs, and (2) that the temperature where rapid growth begins
is lower, the lower the degree of deformation. Grain growth in
reheated, strain-hardened metal probably proceeds by a process
of absorption. The recrystallized grains, relatively strain-free,

and thus more stable than the still distorted ones, grow by absorbing the latter. The atoms of the old grains readjust their positions on their distorted lattices so as to conform to the
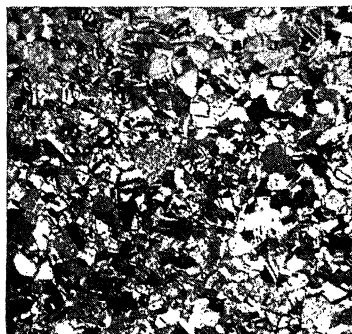
FIG. 164a.—Copper–zinc alloy (alpha brass). 33 per cent reduction. Annealed ½ hr. at 340°C. 100×. Hardness = 65. (*Photograph by Students in Harvard Metallurgical Laboratories.*)

FIG. 164b.—Same as *a* but annealed ½ hr. at 480°C. Hardness = 59. 100×. (*Photograph by Students in Harvard Metallurgical Laboratories.*)
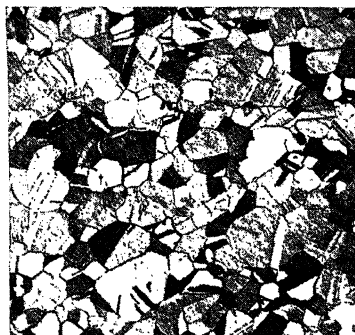
FIG. 164c.—Same as *a*, but annealed ½ hr. at 620°C. Hardness = 55. 100×. (*Photograph by Students in Harvard Metallurgical Labora-*

FIG. 164d.—Same as *a*, but annealed ½ hr. at 760°C. Hardness = 51. 100×. (*Photograph by Students in Harvard Metallurgical Laboratories.*)

orientation of an abutting recrystallized grain whose lattice is comparatively strain-free. Thus these atoms gain, at once, a new orientation and a comparatively strain-free environment. The reason why grain growth proceeds generally more rapidly

at higher annealing temperatures is the greater mobility of the atoms under these conditions; the supposed reason why excessively large grains are commonly associated with low degrees of deformation is that few recrystallizing centers start in such metal.

The effect of the temperature of anneal on the grain size of cold-worked alpha brass (for photomicrograph of the brass as cold-worked, see Fig. 140c) is shown in Fig. 164. The time of annealing ($\frac{1}{2}$ hr.) was the same in each case, and the amount of cold work (24 per cent reduction of area) was also identical in all. Further illustrations of time and temperature effects on the grain size of annealed metal are shown in Fig. 165. In the first column are given the photomicrographs of three cold-worked sheets after annealing for 1 hr. at 815°C. The specimens were air-cooled, so that they were exposed to the high temperatures only during the 1 hr. sojourn at the maximum temperature, plus, of course, the time taken to come up to this temperature. Recrystallization has occurred in all of these cases. The grain size is fairly small and uniform in each sample. Furthermore, it is the same in all samples with perhaps some indication that the most severely deformed specimen has, on the whole, a slightly smaller size of grain. In the second column are photomicrographs of the same sheet annealed for 1 hr. at 925°C., and again air-cooled. The grain size is somewhat larger than in the preceding case. The next column's photomicrographs illustrate, when compared with those of the second column, the effect of time on grain size. The specimens photographed here were all furnace-cooled in a commercial-size annealing furnace, which required several hours to reach room temperatures. Consequently, the time that the steel was exposed to grain-growing temperatures was much longer here than in the preceding cases where the samples were taken from the furnace immediately after the 1 hr. heating. The grain size is definitely larger than the air-cooled samples annealed at the same temperature.

The photographs in the right column illustrate the effects of a curious phenomenon, a case of "exaggerated grain growth." The previous illustrations, diagrams, etc., which relate grain size, degree of deformation, annealing temperature and time, assume uniformity in the degree of deformation and in the temperature of the specimen. When both of these two condi-
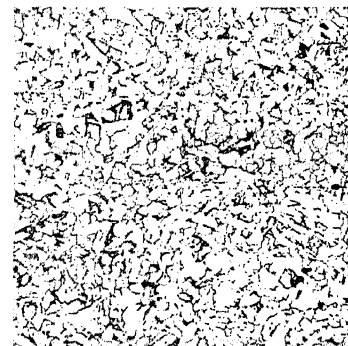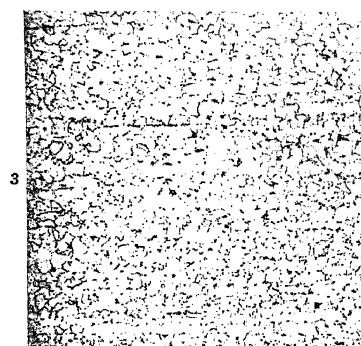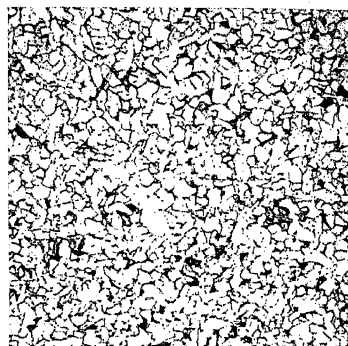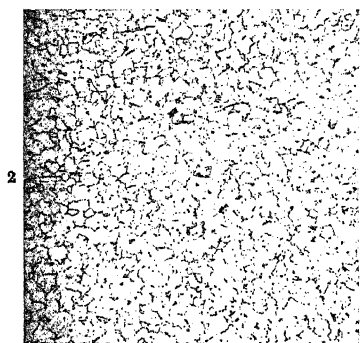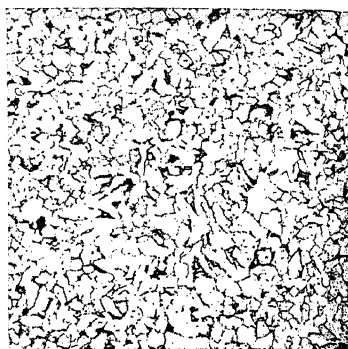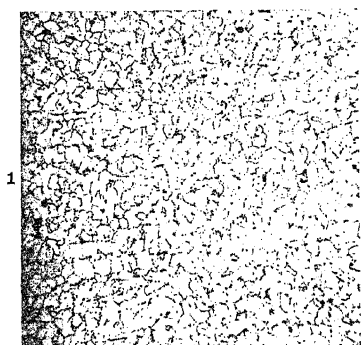
Annealed at 815°C. for 1 hr. Air cooled.

Annealed at 925°C. for 1 hr. Air cooled.

1. Slightly cold-worked.   2. Moderately

FIG. 165.—Grain growth in annealed
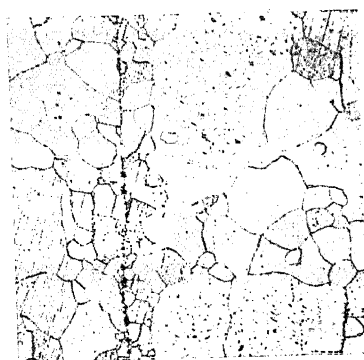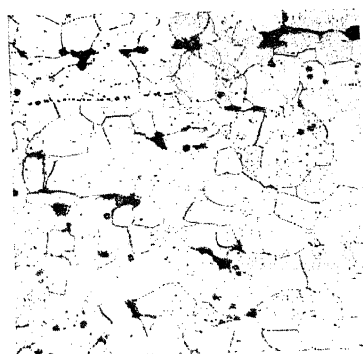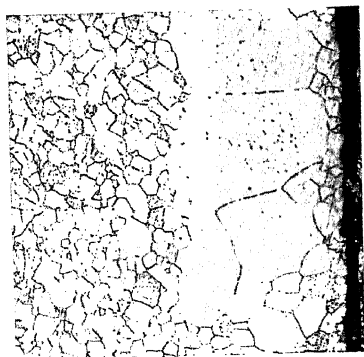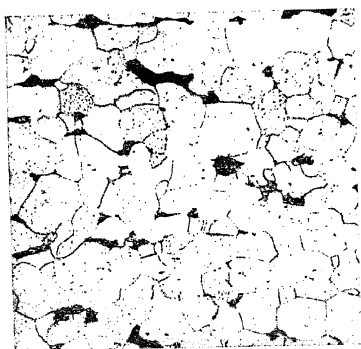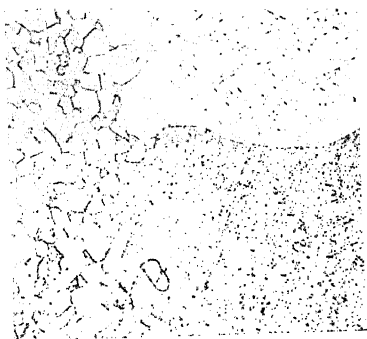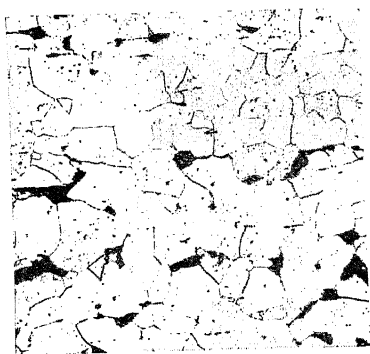
Annealed at 925°C. for 1 hr. Furnace
cooled.

Annealed at 760°C. for 1 hr. Furnace
cooled.

cold-worked.   3. Severely cold-worked.
strain-hardened low-carbon steel.   100 ×.

tions prevail, we have what may be called normal grain growth. When, however, either a strain gradient or a temperature gradient exists in the specimen, and at the same time a critical complementary condition (temperature or degree of strain) prevails, grain growth may be greatly accelerated over what is the normal rate. These three photographs were taken along the edge of the sheet, near one surface (the surface shows at the right-hand edge of one photograph). A strain gradient evidently existed in each of the preannealed sheets, due presumably to the circumstance that deforming stresses applied on the rolling
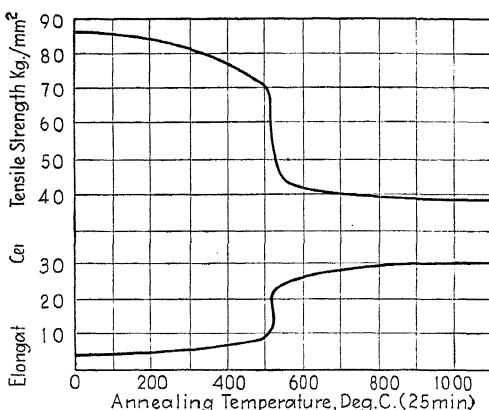
Fig. 166.—Change in mechanical properties of hard-drawn ingot iron (0.08 per cent C) on annealing for 25 min. (*After Schmid and Boas.*)

surface of the sheet did not act with the same effectiveness somewhat below the surface as they did right on the surface. Consequently, a nonuniform distribution of strain from outside to center existed at the time of the annealing. The temperature of 760°C., or thereabouts, seems to have been critical, since definitely higher temperatures, *e.g.*, 925°C., were not particularly effective and it can be shown that lower temperatures are even less so.

The abnormal type of grain growth on annealing has been observed in a number of alloys (mild steels, silicon steel, brasses, etc.). The phenomenon, if prominent at all, is accompanied by an impairment of the toughness properties and is known in the case of the steel as Stead's brittleness.

Property Effects of Annealing.—It has been stated that the annealing of cold-worked metal is rehabilitative in intent and consequences; the properties which were changed in one way or another by cold-working are restored to the metal. In the annealed series of brasses (Fig. 164), the hardness change from 95, the hardness of the cold-worked metal shown in Fig. 140c to 65–51, (depending on the temperature of annealing) of the annealed alloys affords a simple case of property change on annealing of cold-worked metal.

The change in mechanical properties of a hard-drawn ingot iron on annealing at various temperatures for 25 min. is shown in Fig. 166; the changes in tensile strength for annealed brass sheet, previously rolled to four different reductions, are given in Fig. 167. In all cases the property change waits on a sufficient temperature, *i.e.*, the recrystallization temperature, then occurs rapidly over a temperature range, eventually proceeding very slowly or not at all. The direction of change on anneal-

Fig. 167.—Effect of annealing at various temperatures on brass sheet previously deformed 15, 30, 50, and 75 per cent.

ing is, of course, opposite to that on cold-working, the strength properties decrease, and the plastic properties increase.

The electrical, magnetic, and corrosion-resistance properties of strain-hardened metal are also "normalized" by annealing. The time-temperature-resistance–change diagram of strain-hardened copper is shown in Fig. 168. In Fig. 169 are given two diagrams which show the relative magnitude and the distribution of the stresses in a nickel steel, first, in the cold-drawn condition, and then after this has been annealed. The release of internal strain is practically complete by such treatment. Strain relief and fine-structure effects of annealing are also evident in the X ray photographs of Fig. 170a; full description accompanies each photograph; but in general we may say that as the temperature of annealing increases, the internal strain

and the directed orientation become less and less, while the sizes of the recrystallized grains become larger and larger.

The Solution and Precipitation Anneals (the Age-hardening Treatment.—An example of the age-hardenable alloys used as an illustration above, the quenched gold-copper alloy was susceptible to fundamental changes on reheating which affected the hardness because the alloy was structurally unstable. This instability was the consequence of *supercooling.* A more common source of structural instability which likewise leads to age-hardening is *supersaturation.* A type equilibrium diagram of such an alloy system showing age-hardenable properties is given
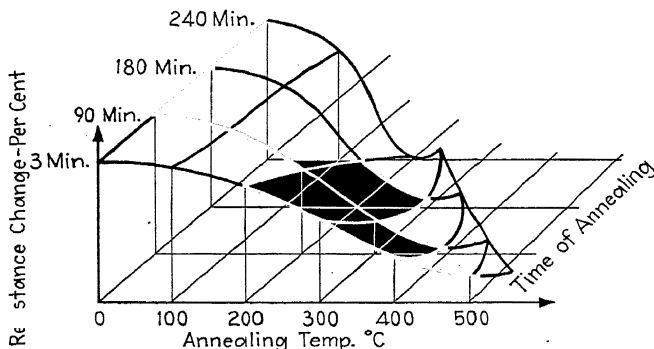
Fig. 168.—Diagram showing the change in the electrical resistance of hard-drawn copper wire on annealing at various temperatures for various lengths of time. (*After Sachs.*)

in Fig. 171. We have a terminal solution which shows a varying solubility with temperature. At room temperatures, metal *A* can dissolve *a* per cent of *B*, at the higher temperature *t*, the solubility is increased to *b* per cent. The solubility at any intervening temperature is given by points along the line *a-b*. Any slowly cooled alloy intermediate between the maximum and minimum solubility values, as, for example, (*x-x'*), consists at room temperatures of the *A*-rich solution containing *a* per cent of metal *B*, and a second constituent, a new phase which contains the excess *B*. The nature of this second constituent is determined by what the next phase is in the particular alloy series; commonly, but not always, it is intermetallic compound. When the duplex alloy is slowly heated, the second

constituent is gradually dissolved by A; at temperature t_1, solution is complete.   If this alloy is then recooled slowly, reprecipitation of the second phase occurs.   But if the cooling rate is such as to deny the time necessary, whatever that may be, for reprecipitation to occur, the rapidly cooled alloy will retain in solid solution
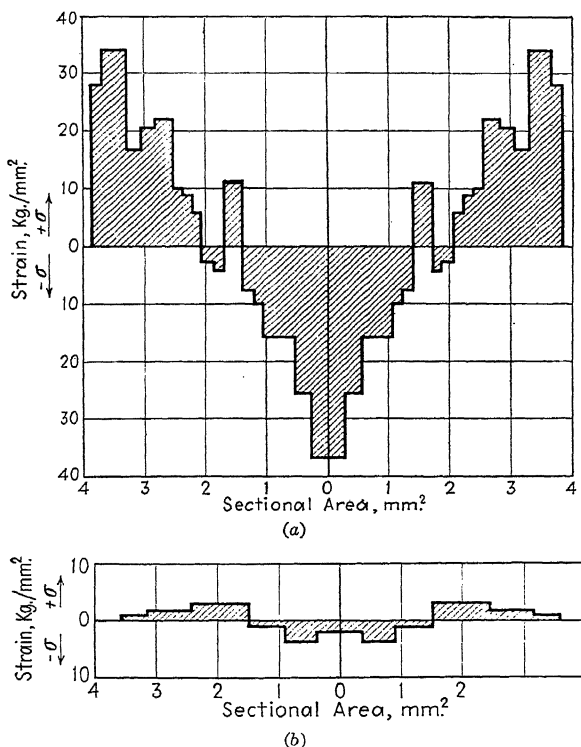
FIG. 169.—Distribution of internal stresses in a drawn nickel-iron-carbon alloy. (a) As cold drawn; (b) after annealing 1 hr. at 850°C.   (*After Sachs.*)

at room temperatures more than the equilibrium amount of B; the solution will be supersaturated and hence unstable.   A reheating of this unstable alloy to temperatures below t_1 will permit the suspended precipitation to proceed, and the alloy reverts to a stable condition and the solution to one of normal concentration.   If the reheating operation, as regards the time and the temperature, is such that the rejected phase is pre-

Fɪɢ. 170*a*.—Copper sheet, cold-rolled. Small grain, considerable internal strain, and some directed orientation.
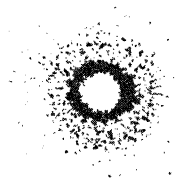
Fɪɢ. 170*b*.—Same cold-rolled copper sheet as above, but annealed at 400°C. Somewhat larger grain size than the rolled sample, indicating that recrystallization has occurred. Some internal strain, no evident directed orientation.

Fig. 170c.—The same sheet annealed at 750°C. Larger grain size than the preceding sample. No strain.
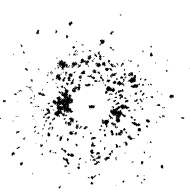
Fig. 170d.—The same sheet annealed at 1000°C. Very large grains.

cipitated in particles of critical dimensions, age-hardening effects will follow.

Such an age-hardening system is the copper-beryllium system. The equilibrium diagram of this system is one of the type illustrated in Fig. 171. The maximum solubility of beryllium in solid copper is around 2.5 per cent (given also as 2.8 per cent), at a temperature of 800°C.; at 400°C. it is around 0.75 per cent, and at room temperatures it is certainly less, but the exact figure is indeterminate. This constitutes the alpha solution of the series; the second phase, a beryllium-rich phase, is another solution, called gamma. If, for example, the 2.5 per cent beryllium alloy is heated to somewhere about 800°C., where all of the beryllium is dissolved (s o l u t i o n annealing), and quenched from that temperature, a definitely supersaturated alpha solution results. Reheating this quenched alloy to temperatures within the range of 200 to 400°C. (precipitation annealing) results in the precipitation of the gamma solution, with changes in hardness as shown in the several hardness-time curves of Fig. 172. The age-hardening behavior of this alloy is generally like that of the gold-copper alloy, including a failure to develop maximum hardness at the lower precipitation annealing temperatures except over abnormally long time periods, and overaging effects at the higher temperatures, etc.

171.—Temperature-solubility relationships in an age-hardening system.

The first definitely recognized age-hardenable alloy was an aluminum alloy containing essentially 4 per cent of copper (duralumin). This alloy has an uncommon aging characteristic (which, in fact, led to the discovery of its age-hardening properties), *viz.*, the quenched alloy ages at temperatures as low as room temperatures. The mechanical hardness changes which take place in this alloy were explained originally as due to the keying effect of discrete particles of copper aluminide ($CuAl_2$) which were precipitated along potential slip planes of the alloy.

These increase the hardness because they increase the resistance to slip. But later it was found that properties other than the simple mechanical properties were implicated in the age-hardening of this alloy, and that these, in the case of the room-temperature-aged duralumin, were not explainable by the simple precipitation hypothesis. For example, the electrical conductivity of duralumin aging at room temperatures slightly decreases, an effect opposite to what actual precipitation should lead. The conductivity of dilute solid solutions decreases with increased concentration of the solute, so precipitation of the solute, as is
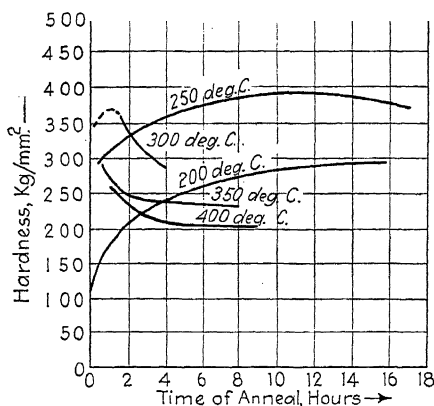
Fig. 172.—Hardness-time curves found in the aging of a 2.5 per cent Be copper-beryllium alloy. (*After Hessenbruch.*)

assumed to happen on aging, should increase the conductivity. Also, the lattice parameter of duralumin remains unchanged when aged at room temperatures. When copper is dissolved in aluminum, the constant of the lattice of aluminum gradually decreases; aging, if it is a dilution process, should result in an increase of this constant. But there is no change.

However, on aging quenched duralumin at higher temperatures, 150 to 200°C., the increase in mechanical hardness is always accompanied by the expected, if slight, changes in conductivity and in lattice constant. Apparently, the aging mechanism in the two cases is somewhat different. It would seem that the original explanation given for the hardening of duralumin, *viz.*, the keying effect of precipitated particles of

critical dimensions, is applicable only to the alloy when aged at high temperatures, for then only does the theory fit in with anywhere near all of the observed phenomena. The aging behavior of duralumin at ordinary temperatures calls for a modification of this theory. It is now claimed that aging at room temperatures does not result in actual precipitation of the solute atoms—apparently the temperatures are too low for the process to proceed that far—but that these atoms, which are about to do so, collect in small groups locally on the host lattice, constituting with the proper number of the host metal's atoms, potential crystal nuclei—crystals *in embryo*. It is a case where precipitation is imminent but not actual, threatening but not a fact. Localized segregation of the solute atoms on the solution lattice results conceivably in distortion of the latter in the vicinity of each of the incubating crystals. An increased resistance to slip along the roughened planes is a consequence, and the internal strain incident to distortion increases the electrical resistance. Since all solute atoms are still in solution, there is no change in the lattice constant of the solution.

The Copper-nickel-silicon System.—The alloys at the copper corner of this ternary system are examples of age-hardenable alloys. Copper and nickel alone form a continuous series of solid solutions; they are mutually soluble in all proportions in the solid state. The addition of small amounts of silicon changes, in a marked degree, this solubility relationship. The nickel and the silicon form an intermetallic compound, Ni_2Si, which shows limited solubility in copper, the exact solubility depending on temperature. The copper corner of the ternary diagram (Fig. 173) gives a maximum solubility of the silicide in copper of a little less than 9 per cent. This is at a temperature of about 1100°C.; the solubility at 300°C. is, however, less than 1 per cent, and at room temperatures it is probably still less. The second constituent in this series, at the copper corner, is the silicide compound.

The particular alloy composition, whose age-hardening curves are given in Fig. 174, contains 2.08 per cent Ni_2Si, the specific percentage composition of the alloy being copper 97.78 per cent, nickel 1.77 per cent, and silicon 0.40 per cent. The solution-annealing treatment consists in heating the alloy to 775°C. for 1 hr.; this treatment suffices to put all the silicide

into solution. Water quenching from the solution-annealing temperature is a sufficiently rapid cooling to retain the silicide in solution. The hardness of the quenched alloy is 54 (Rockwell *B*). The precipitation annealing temperature ranges from 300° to 700°C. In the lower set of curves of Fig. 174 the hardness of the sample aged at 475°C. reaches its maximum hardness in about 8 hr. Practically the same hardness is obtained in the 500°C. anneal in 3 hr., and in 1 hr. at 525°C. Annealing at 550°C. never develops a maximum as high as those secured in the lower anneals, and in the 700°C. anneal the hardness drops from the start. Overaging, the result of particle growth beyond
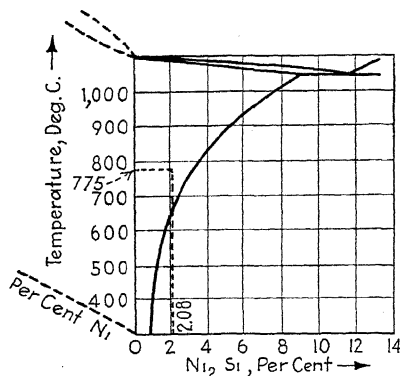
Fɪɢ. 173.—The copper corner of the copper-nickel-nickel silicide ternary diagram. (*After Corson.*)

critical size, is found in all cases, being most prominent in the samples annealed at the higher temperatures. The upper curves of the figure tell the story of hardness changes during longer annealing periods. It is, however, the same story as the curves of the 0- to 20-hr. range of aging tell.

The electrical conduction changes during aging of the alloy indicate that actual precipitation of the solute occurs. The data, in terms of pure copper's conductance, are given in Table 25.

The Hardening of Steel.—The hardening of steel is essentially a dispersion-hardening phenomenon, differing certainly from the preceding examples in the magnitude of the hardening effects and apparently also in the complexity of the mechanism
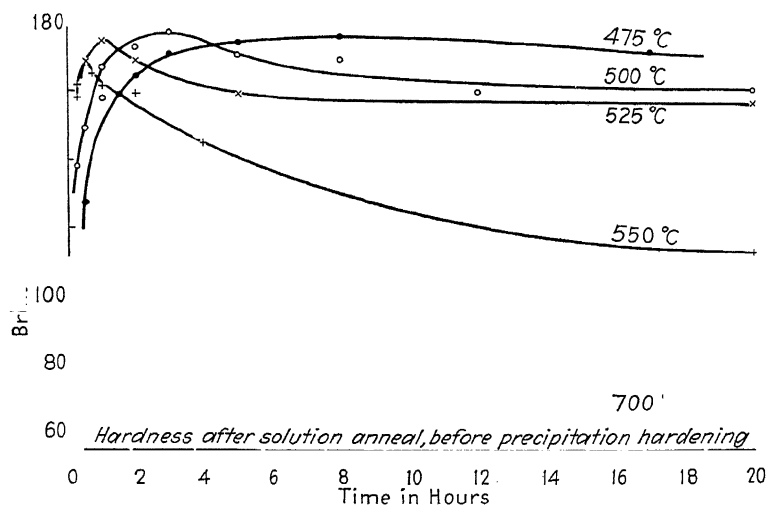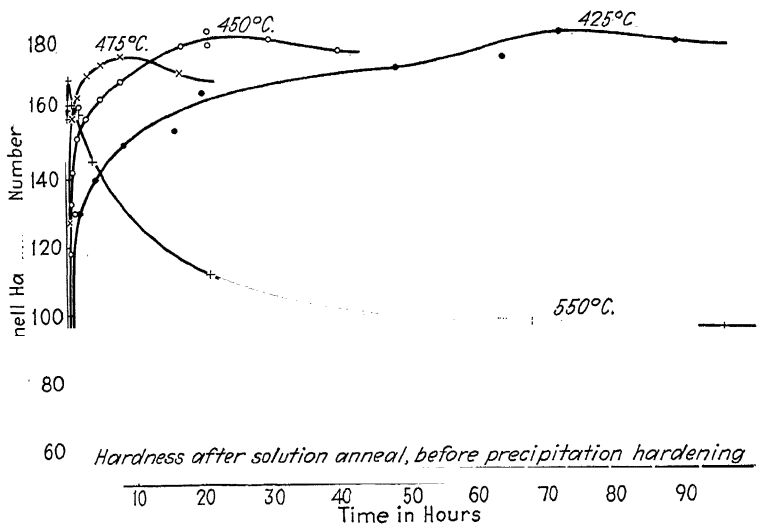
FIG. 174.—Effect of aging time at various temperatures on the hardness of the 2.08 per cent Ni₂Si copper-nickel-silicon alloy. Above, the 0–100 hr. range; below, the 0–20 hr. range. (*After Gonser and van Wert.*)

responsible. In Fig. 175 is given a simplified form of the iron-carbon diagram, showing only the information immediately concerned in the heat-treatment of plain carbon steels.

TABLE 25.—EFFECT OF AGING TREATMENT ON THE CONDUCTANCE OF THE 2.08 PER CENT NI$_2$SI COPPER-NICKEL-SILICON ALLOY

Condition	Hardness	Per cent conductance of copper
Solution annealed	56	18.27
Partly aged......	142	30.13
Fully aged.......	173	40.96
Overaged........	113	42.20
Annealed........	85	34.27

Let us confine our attention to the steel composition of 0.9 per cent carbon, *i.e.*, the one of eutectoid composition. Above the V-shaped eutectoid-inversion curve, the solid solution of carbon in gamma iron (austenite) is the stable phase. This is true for
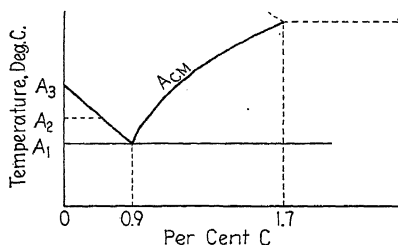
FIG. 175.—Simplified portion of iron-iron-carbide equilibrium diagram of use in the heat-treatment of steel.

all compositions, including the one under consideration. The solubility of carbon in gamma iron is considerable (for an interstitial solution), being 1.7 per cent at a temperature of about 1140°C., the melting point of the eutectic, and about 0.90 per cent at the eutectoid inversion temperature of 700°C. On slow cooling through 700°C., the gamma iron, no longer able to delay further the much overdue transformation (it already has been undercooled 200°C., through the stabilizing presence of 0.9 per cent of carbon) changes to alpha iron (ferrite); and because the

solubility of carbon in ferrite is extremely small (0.03 per cent, perhaps, at 700°C.), the carbon is rejected from the iron lattice in the form of an iron-carbon compound, Fe_3C, cementite. The simultaneous precipitation of ferrite and cementite from austenite on slow cooling through the critical range of temperature results in the formation of a duplex aggregate, called pearlite, photomicrographs of which have been shown earlier (see also Fig.

FIG. 176a.—0.85 per cent carbon steel, slowly (furnace) cooled through the critical range. Pearlite. 1000×. *(Photograph by Reed.)*

FIG. 176b.—0.85 per cent carbon steel, quickly cooled (water-quenched) through the critical range. Martensite. 500×. *(Photograph by Reed.)*

176a). The pearlitic aggregate (with excess, pro-eutectoid ferrite for hypo-eutectoid compositions, excess cementite for hypereutectoid alloys, but at the eutectoid composition, pearlite alone) is the product of the slow transformation of austenite, where everything that is due to occur is given all the time it needs to occur. And we must remember that there are at least two things that do occur (considering only the initial and the final states of the alloy): first, the change in lattice from a face-centered cubic to a body-centered one, and second, the precipitation of the carbon as an iron carbide. Now, what happens if the

time needed for these two simultaneous changes to occur is denied, that is to say, if the cooling through the critical temperature is markedly accelerated as by water quenching?

If by "what happens" we mean what changes in properties take place, the question is easily answered, for one can readily determine that the strength properties of the steel are considerably increased by the quenching treatment while the plastic
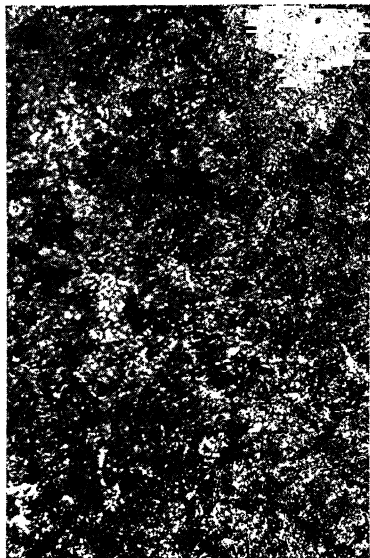
FIG. 176c.—0.85 per cent carbon steel. Water quenched from 825°C., and reheated (tempered) to 400°C. T r o o s t i t e. 500 ×. (*Photograph by Reed.*)

FIG. 176d.—0.85 per cent carbon steel. Water quenched from 825°C., and reheated to 650°C. Sorbite. 500 ×. (*Photograph by Reed.*)

properties become seriously impaired. If however, we refer to microstructure changes, the answer must be less definite, for while we secure a characteristic microstructure in the quenched alloy, known as martensite (see Fig. 176b), the fineness of the structure presents difficulties in the way of resolution; its general cleavage character, however, tells us something about the crystallographic relationship of the new structure with the parent austenitic one. But if by our question we inquire concerning the changes in the fine structure of the alloy, partic-

ularly as these affect the final form and distribution of the carbon, any positive answer is hazardous. We do know, of course, the crystallographic form of the iron before quenching, and we do know the form of the iron after quenching, for martensite is predominantly body-centered cubic. But the path traveled from the one to the other condition is not so surely known, but evidently an intermediate tetragonal form of iron, unstable and of inconstant c/a ratio, exists, for this form of iron
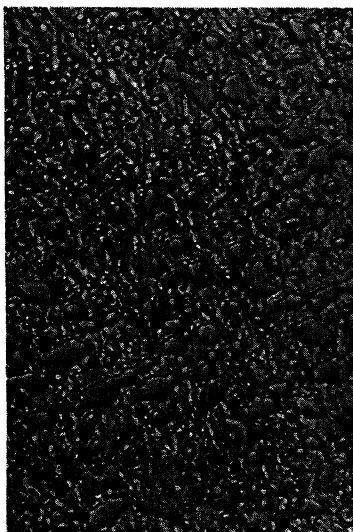
Fig. 176e.—Steel of slightly hypereutectoid composition, fully spheroidized.   500×.   (*Photograph by Reed.*)

has been found in quenched steels (Fig. 177). Presumably, this is a trapped transitional form of iron. What actually happens to the carbon during this reorganization of the iron lattice is still more uncertain, and we are not even sure of its final condition. Probably, it is in the form of extremely finely dispersed particles of iron carbide, yet, as is assumed in the case of low-temperature aged duralumin, it may be that precipitation is impending rather than having actually taken place. Because the change in the iron from the gamma to the alpha form occurs with so little lapse of time, in fact almost instantaneously, the recrystallized alpha grains have no time to grow; they remain almost with nuclear dimensions. This is also conceivably true of the trapped particles of any precipitated cementite. And because the ferritic crystals, like all other recrystallized grains, will grow if opportunity is given, they are apparently strained. Martensite seems, then, characterized by an extremely small grain size of the continuous phase (ferrite), whose individual units possess internal strains of some significant magnitude due to the unusual time-temperature conditions under which they formed, and to the presence of critically dispersed particles of cementite without, or to embryonic crystals of the carbide within the ferrite lattice.

Yet, it has been impossible to determine which of these characters peculiar to martensite is the predominant cause of its exceptional hardness.

Martensite, like any fully aged alloy—if such it is—is susceptible to overaging. If the quenched alloy is reheated to low temperatures, the hardness decreases and the toughness properties proportionately increase, presumably because the grains and the particles of the martensitic matrix grow somewhat in size and the crystallites lose some of their strain. This constitutes *tempering* or *drawing*. If the reheating or tempering temperatures are low, say in the neighborhood of 400°C. (though particular temperature effects are a function of time), martensite changes into a quite microscopically structureless, easily etched complex, known as *troostite* (see Fig. 176c), somewhat
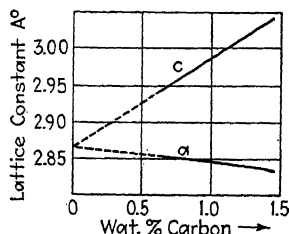
FIG. 177.—Lattice cons tetragonal martensite as _ _ _ tion of carbon content. (*After Öhmann.*)

softer but much tougher than martensite. This is tempered steel, and is ordinarily the useful condition of so-called hardened steel since it possesses a much better combination of hardness and toughness than does the simply quenched variety. Heating to higher temperatures results in further drop in hardness and gain in ductility and toughness. Grain and particle size obviously continue to increase. The microstructure obtained does not differ decidedly from the troostitic structure, and a definitely resoluble structure fails to develop, though slight differentiation of constituents is at times discernible. Etching, however, is much less rapid, than in the case of troostite. This structure is known as *sorbite* (Fig. 176d). Prolonged heating at temperatures just below 700°C. results eventually in the formation of microscopically visible cementite particles; in fact, these carbide particles may be made to assume spheroids of rather large size (Fig. 176e). This is the condition known as *spheroidization*.

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